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REPORT No. 10

SMALL ARMS PRIMERS

By

Ernest R. Rechel
Junior Chemist

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ORDNANCE LABORATORY
FRANKFORD ARSENAL
PHILADELPHIA, PA.

March, 1932

REPORT NO. 10.

SMALL ARMS PRIMERS

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CONTENTS

	<u>PAGE</u>
I. INTRODUCTION	1 - 3
II. EXPERIMENTAL COMPOSITIONS.	3 - 21
Ingredients.	3
Method of Dry Mixing.	4
Method of Wet Mixing.	4
Loading	4
Testing	4 - 6
Mercury Fulminate Compositions.-	6
1. Use of Strontium Nitrate and Lead Nitrate in Place of Barium Nitrate.	6
2. Use of Cuprous Sulfocyanite in Place of Lead Sulfocyanide.	7
3. Pretreatment of Barium Nitrate.	7 - 8
4. Use of Tetracene in Place of Mercury Fulminate.	8
5. Lead Styphnate and Lead Picrate Mixtures.	8
6. Varying the Granulation of the Barium Nitrate and Antimony Sulfide.	9 - 10
7. Varying the Ratio between Lead Sulfocyanide and Antimony Sulfide.	10 - 11
8. Zirconium Mixtures.	12 - 15
9. Varying the Granulation of the Mercury Fulminate.	15 - 16
Potassium Chlorate Compositions.-	16
1. Pretreatment of Potassium Chlorate.	16 - 17
2. Tetracene Mixtures.	17
3. Varying the Granulation of Potassium Chlorate and Antimony Sulfide.	17 - 18
4. The Relative Importance of Antimony Sulfide and Lead Sulfocyanide in the F. A. 70 Mixture.	19
Non-corrosive Non-fulminate Compositions.-	20
1. Rathsburg Compositions.	20 - 21
2. Diazol Compositions.	21
III. THEORY.	21
General.	21 - 22
Granulation.	22 - 28
Coefficients of Friction.	28 - 31
Ignition Temperatures.	31 - 35
The Primer Flame.	35 - 39

I. INTRODUCTION.

The following report deals with work that has been pursued at Frankford Arsenal during the last two years on the development of non-corrosive priming mixtures. The program of experimental work as originally planned was very much amplified as the work went on. For this reason no report was issued at the end of the first year, at that time some of the more interesting implications of the problem were beginning to be grasped, and it was decided to postpone the date of report.

The most remarkable thing about the history of percussion primers is the total absence of any radical changes or brilliant improvements, since their invention, such as have occurred in the field of propellant powders. Modern primers are very much the same as the first primers made by Forsyth in 1807, containing 70.6 parts of potassium chlorate, 11.8 parts of charcoal, and 17.6 parts of sulfur. Important improvements have been made in the uniformity and reliability of primers, but the priming charge still consists, as it has for the last century, of a heterogeneous mixture of granular substances, capable of taking fire when struck. The remark has frequently been made that primers are still in the "black powder" stage of development.

The first improvement on Forsyth's primer came in 1819 when Wright used a mixture of mercury fulminate, potassium nitrate, sulfur, and black powder (1). Many persons, however, still favored the chlorate primer because of its safety in handling, and so Dreyse came forth with a mixture of 52.4 parts of potassium chlorate and 47.6 parts of stibnite, or antimony sulfide. Dreyse's mixture must have been very insensitive, even when compared with Forsyth's mixture, for after awhile mercury fulminate was added, and a priming mixture was produced which was satisfactory enough to remain in use many years. Many governments still use this mixture, or modifications of it, in their ammunition. Powdered glass is frequently used to increase the sensitivity, and a binding material such as shellac, gum, or gelatin, is usually added to hold the separate ingredients together. One of the Austrian primers (1) (2) may be quoted as representative of this type of mixture, being composed of:

Mercury fulminate	13.7%
Potassium chlorate	41.5%
Antimony sulfide (stibnite)	33.4%
Powdered glass	10.7%
Gelatin	0.7%
	<u>100.0%</u>

The United States Army used a fulminate mixture as late as 1899, but eventually changed to the chlorate, non-fulminate type which has gradually been improved until today it is probably the best primer from a ballistic standpoint that has so far been evolved. The fulminate is eliminated through the use of more easily ignited fuels, thereby increasing the sensitivity of the mixture, so that it compares very well with mercury fulminate mixtures. The composition now being loaded at Frankford Arsenal is the well known Winchester, or F.A.70, mixture:

Potassium chlorate	53%
Antimony sulfide	17%
Lead sulfocyanide	25%
T.N.T.	5%

This composition is moistened with a small amount of gum solution and then loaded in the usual way. In this composition the T.N.T. and lead sulfocyanide are the easily ignited fuels which give the primer the required sensitivity. In place of these, the sulfocyanides, ferrocyanides, and thiosulfates of various heavy metals have also been proposed for priming mixtures.

During recent times a third type of primer has been the object of much experimental work. It contains neither fulminate nor chlorate, and depends for its ignition on any one of several explosive compounds. It is, perhaps, the "ideal" type, since it attempts to avoid the bad features of the fulminate and chlorate primers. But none of the mixtures belonging to this third type have been used extensively, and whatever advantages they may seem to have are offset by the fact that very little experience has been had with them.

At present then, there are two types of priming mixtures which are known well enough to merit consideration for service ammunition. These are the mercury fulminate primer without chlorate and the potassium chlorate primer without fulminate. Each, however, has serious disadvantages. Mercury fulminate is somewhat dangerous to work with, it constitutes a constant menace to life and health. The chlorate primer, on the other hand, is quite safe to manufacture, but its great disadvantage is in the marked rusting caused by chlorate residues in rifles, necessitating prompt and frequent cleaning of the barrels (3) (4). Ballistically, the chlorate primer is far ahead of all other types. The use of machine guns synchronized with airplane propellers in modern warfare places rigorous limitations on the amount of hangfire that can be allowed in aircraft ammunition, and in this respect the chlorate primer is very

reliable. Hangfires are very rare, indeed, with the F.A.70 composition. But fulminate primers show a persistent tendency to hangfire, and in the opinion of many this is their chief disadvantage. At least, this is the one disadvantage that would certainly prevent their adoption for service ammunition. We have then, on the one hand, the chlorate primer with its good ballistics and bad corrosive effects, and on the other hand, the fulminate primer with its non-corrosive features and bad ballistics. This, briefly, is the situation now existing with regard to small arms priming compositions.

The present work has been directed mainly toward the elimination of hangfires in non-corrosive primers. Much attention has also been given to the theoretical side of the problem in an attempt to discover what conditions tend to produce hangfires. The report, therefore, has been divided into two main parts: the first part describing the mixtures prepared and the ballistic results obtained from them, and the second part setting forth theoretical considerations regarding the composition and functioning of primers. These investigations have been confirmed exclusively to the primer used in .30 caliber ammunition, and the conclusions drawn will, of course, relate only to the .30 caliber primer.

II. EXPERIMENTAL COMPOSITIONS.

Ingredients

With two exceptions, all the ingredients used were very pure chemical compounds equivalent to "C.P." grade. The mercury fulminate, however, was of the usual purity used in detonators and primers; that is, it contained about 99% mercury fulminate. The antimony sulfide consisted of ground stibnite, containing approximately 90% Sb_2S_3 this grade being regularly used for priming compositions.

The granulation of each ingredient was controlled by means of four standard Tyler sieves of 80, 100, 150, and 200 mesh. The following convention has been adopted for indicating the fineness of the various ingredients:

- 100/150 represents material which passed through the 100 mesh sieve but was retained by the 150 mesh sieve.
- /80 represents material coarser than 80 mesh, upper limit of coarseness unknown.
- 200/ - represents material finer than 200 mesh, lower limit of fineness unknown.

Method of Dry Mixing

In making up a priming composition for dry charging, the ingredients are weighed separately and then mixed by passing them twice through an 80 mesh sieve. A brush is used to break up lumps if any are formed. If explosive compounds, such as mercury fulminate, are to be used in the mixture, they are laid aside until the other materials have been sieved. The explosive material is then added and the whole thoroughly blended by "rolling" the mixture on clean paper. All priming mixtures loaded dry are distinguished by having the letter "D" added to the serial number.

Method of Wet Mixing

In preparing mixtures for wet charging, the ingredients are first mixed dry, the same procedure being used as for dry charging. The mixture is then poured upon a clean glass plate and enough gum solution added to give it the proper consistency. The gum solution is worked in by hand, and after thorough mixing, the composition is placed in hard rubber boxes and covered with a damp cloth. All the experimental wet mixtures were loaded within three hours after they were prepared. The gum solution is composed of:

Gum Tragacanth	60 parts
Gum Arabic	110 "
Gluo (1- $\frac{1}{4}$ Test, Cooper's)	10 "
Water	3000 "

All priming mixtures loaded wet are distinguished by having the letter "W" added to the serial number.

Loading

All experimental mixtures are loaded on standard machines under production conditions, standard cups and anvils being used throughout. The pellets are, of course, foiled with shellacked paper moistened with alcohol, the anvils being inserted immediately afterward. The primers are then dried at 110° F. for about 36 hours, and at 120° F. for 5 hours.

Testing

After the primers have been dried, a quantity of cases are primed with them, and the primers crimped in. Some of the primed cases are used for the drop-test to determine the sensitivity of the primers. The drop-test is made in the usual way on a standard machine, using a freely falling 4 oz. ball dropped from various

heights. The ball falls upon a firing pin which fires the primer. U.S. Army Specifications require that all .30 caliber primers must fire when the ball is dropped 15 inches, and all must fail to fire when the ball is dropped 4 inches. Under well controlled manufacturing conditions, however, it is possible to narrow the range of sensitivity considerably. At Frankford Arsenal, daily drop-tests on production work show that the present .30 caliber primers fire very consistently at 10 inches and miss at 6 inches. The results of drop-tests on experimental mixtures will be represented graphically, since this facilitates the comparison of mixtures. A separate graph is placed beside each mixture, showing the number of primers fired vs. height of drop in inches. For some mixtures, a dotted line graph is also drawn, showing the number of "squibs" found at each height. A primer that ignites, but burns so slowly that no report is heard, is counted a squib. Normal primers give a loud, sharp report.

If the sensitivity of experimental primers is satisfactory, a hangfire test is made under full machine gun action, firing two bursts of from 50 to 100 rounds each. The hangfire machine consists of a paper disc rotating in front of the machine gun. The disc rotates four times for each round fired, the speed being maintained at approximately 1800 r.p.m. The bullets pass through the disc near its edge, and it is plainly seen that if the ammunition is functioning perfectly, all the bullets will pass through the same hole in the disc. But ammunition never functions perfectly. The separate shots always have slightly different velocities and, as a result, a group of holes will be found along the edge of the disc. According to Army Specifications for service ammunition, any shot that lags behind the first shot in the group by more than 108° of arc, disc speed 1800 r.p.m., shall be counted a hangfire. A shot falling between the main group and the 108° limit is counted a lag. For aircraft ammunition, the requirements are more rigorous. Any shot that lags behind the main group by more than 27° is counted a hangfire. But the results given below have been recorded from the standpoint of service ammunition specifications, so that lags will be recorded up to 108° , beyond that, hangfires. In order to determine the lag of the main group itself, the "zero" position must be determined by firing a single shot with the disc standing still. The distance from the "zero" shot to the beginning of the main group then gives the lag of the main group. In tabulating the results of hangfire tests on experimental mixtures, abbreviations will be used as follows:

- R = Number of rounds fired.
- Z = Lag of main group behind "zero" shot, in degrees.
- G = Spread or extent of the main group, in degrees.

L = Lag of individual shots falling behind the main group not exceeding 108° behind the beginning of the main group, in degrees.

H = Lag of individual shots falling more than 108° behind the beginning of the main group, in degrees.

Mercury Fulminate Compositions

At the time these experiments were begun, the most recent fulminate composition that had been worked on at the Frankford Arsenal was known as the 353-D mixture, of the following composition:

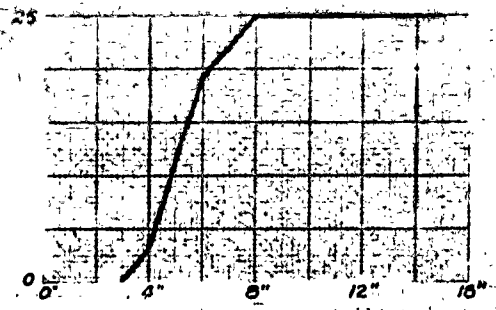
Hg(ONC)2	80/ -	30%
Ba(NO3)2	200/ -	40%
Sb2S3	150/200	20%
Pb(SCN)2	200/ -	5%
T.N.T.		5%

Many of the compositions developed since have been modifications of this mixture, and so 353-D will be referred to frequently as the basic fulminate composition. Its characteristics will be found in Figure 1. It appears somewhat sensitive from the drop-test curve, and the number of lags exhibited is typical. Usually, one or two hangfires will appear in each 100 rounds, although this is not a regular occurrence. This mixture, then, served as a starting point for those described below.

1. Use of Strontium Nitrate and Lead Nitrate in Place of Barium Nitrate.-

It has long been a favorite diversion of people working with priming compositions to attempt to determine the efficacy of mixtures by calculating the amount of heat liberated during explosion. Recent experiments and considerations, to be presented later, suggest that a pellet liberating 15 calories may be superior to one liberating 20 calories, the degree of excellence depending upon several factors of unsuspected importance. However, the benefit of this later experience was not available during the early experiments, and two mixtures were made in an attempt to improve 353-D by using nitrates which give up oxygen with less absorption of heat than barium nitrate. In liberating one gram of oxygen, barium nitrate absorbs 262 calories, thereby cooling the explosion flame by that amount. On the other hand, strontium nitrate will yield the same amount of oxygen with the loss of 234 calories, and lead nitrate will absorb only 140 calories. Strontium and lead nitrates were therefore used in 358-D and 359-D, respectively. The results are in Figure 1.

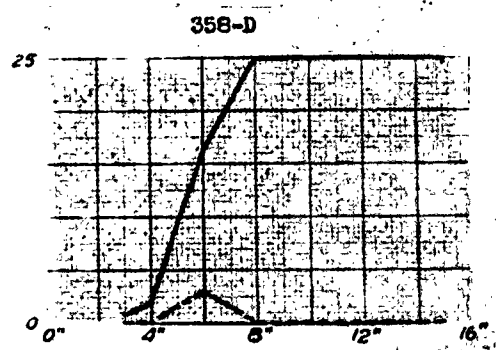
$\text{Hg}(\text{ONC})_2$ 80/- 30%
 $\text{Ba}(\text{NO}_3)_2$ 200/- 40
 Sb_2S_3 150/200 20
 $\text{Pb}(\text{SCN})_2$ 200/- 5
 TNT 100/- 5



R	Z	G	L	H
70	40°	5°	8°	139°
10	42°	5°	13°	
50	40°	9°	39°	

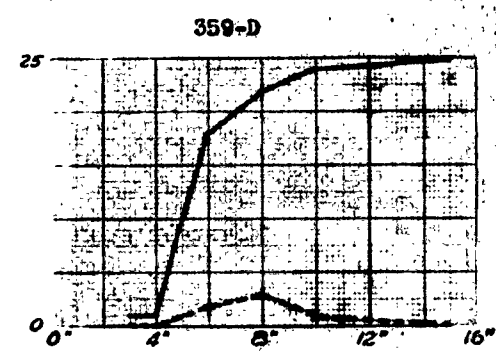
1 misfire

$\text{Hg}(\text{ONC})_2$ 80/- 30%
 $\text{Ba}(\text{NO}_3)_2$ 200/- 40
 $\text{Pb}(\text{NO}_3)_2$ 150/200 20
 Sb_2S_3 150/100 20
 $\text{Pb}(\text{SCN})_2$ 200/- 5
 TNT 100/- 5



R	Z	G	L	H
50	46°	5°	102°	
50	45°	5°		

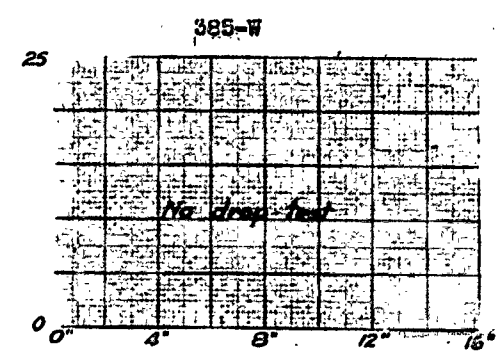
$\text{Hg}(\text{ONC})_2$ 80/- 30%
 $\text{Sr}(\text{NO}_3)_2$ 150/200 40
 Sb_2S_3 150/200 20
 $\text{Pb}(\text{SCN})_2$ 200/- 5
 TNT 100/- 5



R	Z	G	L
50	44°	6°	10°
50	44°	7°	

1 misfire

$\text{Hg}(\text{ONC})_2$ 80/- 30%
 $\text{Ba}(\text{NO}_3)_2$ 200/- 43
 Sb_2S_3 150/200 7
 CuSCN 200/- 15
 TNT 100/- 5



This mixture decomposed so rapidly when wet, it was impossible to load it.

FIGURE 1

In the drop test, one primer from each lot exploded at 3", but this result cannot be ascribed to the new ingredients, since the two primer lots are actually less sensitive than 353-D at 4" and 6", and 359-D is less sensitive at 8" and 10". The hangfire tests also show that nothing has been gained by using nitrates with more favorable thermodynamic properties. The groups are narrow enough, but the tendency to hangfire has not been eliminated. Lot 359-D showed no serious lags or hangfires, but the one misfire that developed is quite as bad as a hangfire. After all, a misfire is simply a hangfire of infinite duration.

Normal lead nitrate would, at any rate, be undesirable in a primer because of its acid reaction. It is understood, however, that one of the loading companies has used basic lead nitrate with some success in priming compositions.

2. Use of Cuprous Sulfocyanide in Place of Lead Sulfocyanide

In 364-D, cuprous sulfocyanide has been used in place of the lead sulfocyanide found in the basic fulminate mixture. The drop test and hangfire test (Figure 2) are very similar to 353-D. Afterwards, another batch of the copper mixture was prepared and loaded wet (364-W). The material was quite unstable when moist and required rapid loading to avoid its setting to a hard cake. Another mixture (385-W) containing 15% cuprous sulfocyanide was prepared, but it decomposed too rapidly and no primers could be charged with it. The formula for 364-W is given in Figure 2, while 385-W is in Figure 1.

3. Retreatment of Barium Nitrate

During the course of miscellaneous experiments on mixtures of various oxidizing agents and fuels, it became apparent that barium nitrate is comparatively sluggish in yielding its oxygen. This has been generally known, and, as mentioned before, is usually accounted for by the fact that in the process of giving up one gram of oxygen, barium nitrate absorbs 262 calories of heat energy. These 262 calories are entirely lost so far as flame temperature is concerned, and combustion is thereby retarded to some extent.

An attempt was, therefore, made to activate the barium nitrate by coating the crystals with a sensitizing material. The method used was to dissolve the sensitizer in acetone, wash the barium nitrate crystals with the solution, and then dry them on the steam bath. A potassium permanganate solution (0.2%) was used in 371-D and 372-D, these mixtures differing in the granulation of barium nitrate. Three other mixtures were made,

373-D, 374-D, and 375-D, in which 1% solutions of T.N.T., P.E.T.N. (pentaerythrite tetranitrate), and picric acid were used, respectively. These five lots are identical in composition with the basic fulminate mixture, with which they should be compared. The results are in Figures 2 and 3.

It is apparent at a glance that no improvement has been made. On the contrary, an unusual number of squibs have appeared, and the hangfires and lags are very conspicuous. In the last three mixtures, where organic explosives were used as sensitizers, a marked drop in sensitivity has taken place. This is just the reverse of the effect these materials have on chlorate mixtures. It should be noted, however, that these five sensitized compositions were loaded dry, and have not been tested as wet mixtures.

4. Use of Tetracene in Place of Mercury Fulminate

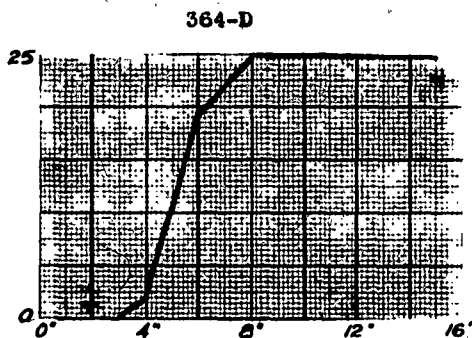
Those who have worked with tetracene (guanylnitros-aminoguanilyltetracene) in primers do not recommend its use as a substitute for mercury fulminate. Nevertheless, one mixture was prepared in which half the fulminate of the basic 353-D mixture was replaced by tetracene. The sensitivity of the composition was apparently unimpaired, but in the hangfire test, the shots were evenly distributed around the entire disc, making it impossible to record a "group" or "zero". Figure 3 shows the formula of this mixture (354-W) and the results obtained. Tetracene is properly used only as a sensitizer, and some results obtained using tetracene in this capacity will appear later.

5. Lead Styphnate and Lead Picrate Mixtures

During recent years attention has been brought once more to lead styphnate as a priming ingredient. This has been largely due to the Rathsburg patents (5) on tetracene mixtures in which lead styphnate is used in place of mercury fulminate. The normal lead salt of styphnic acid is used, and this is prepared by precipitating a solution of magnesium styphnate with lead nitrate. The magnesium styphnate is made by allowing magnesium to react with a solution of styphnic acid, or trinitroresorcinol. This method permits easy control of the crystal size of lead styphnate, and is the generally favored procedure.

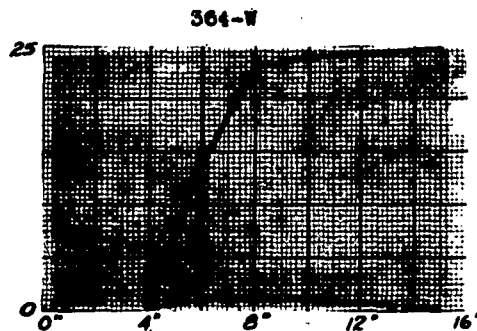
A small quantity of lead styphnate was obtained from the Remington Arms Company for experimental priming compositions. It was used together with mercury fulminate in two mixtures, 388-D and 388-W, in order to discover whether a large increase in the heat of the primer flame would improve matters. It should be pointed out that lead styphnate, like mercury fulminate, is in itself a high explosive. Figure 4 shows the results

$\text{Hg}(\text{ONO})_2$	80/-	30%
$\text{Ba}(\text{NO}_3)_2$	200/-	40
Sb_2S_3	150/200	20
CuSCN	200/-	5
TNT	100/-	5



R	Z	C	L	H
50	46°	11°	70°	142°
50	45°	10°	16°	23°

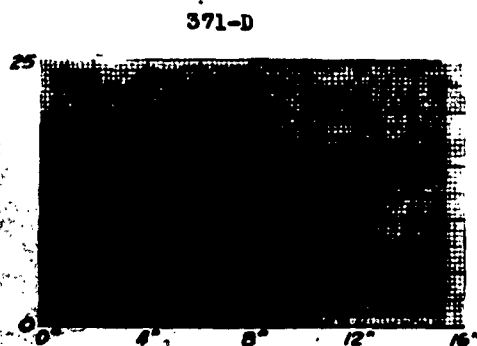
Same composition as 364-D



R	Z	C	L	H
100	44°	15°	26°	120°
100	44°	16°		

$\text{Hg}(\text{ONO})_2$	80/-	30%
$\text{Ba}(\text{NO}_3)_2$	150/200°	40
Sb_2S_3	150/200	20
$\text{Fe}(\text{SCN})_2$	200/-	5
TNT	100/-	5

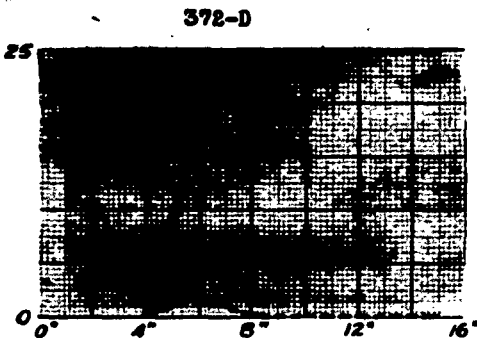
Coated with KMnO_4



R	Z	C	L	H
50	49°	10°	4°	107°
50	49°	5°	6°	170°
			20°	
			21°	
			98°	

$\text{Hg}(\text{ONO})_2$	80/-	30%
$\text{Ba}(\text{NO}_3)_2$	200/-	40
Sb_2S_3	150/200	20
$\text{Fe}(\text{SCN})_2$	200/-	5
TNT	100/-	5

Coated with KMnO_4

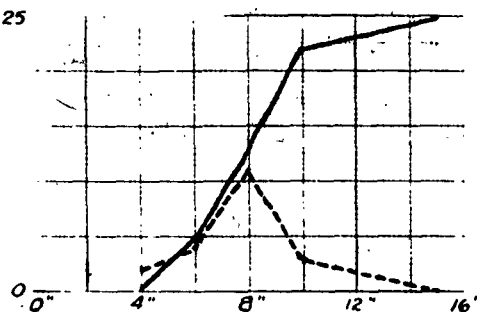


R	Z	C	L	H
50	45°	11°	4°	
50	44°	12°	4°	

373-D

$\text{Hg}(\text{ONC})_2$ 80/- 30%
 $\text{Ba}(\text{NO}_3)_2$ 200/- * 40
 Sb_2S_3 150/200 20
 $\text{Pb}(\text{SCN})_2$ 200/- 5
 TNT 100/- 5

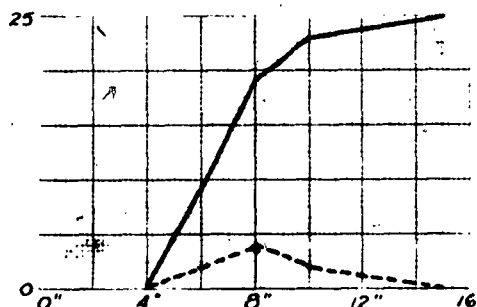
* Coated with TNT



R	Z	C	L	H
50	48°	6°		187°
50	48°	6°		196°
				258°
				335°
				350°

374-D

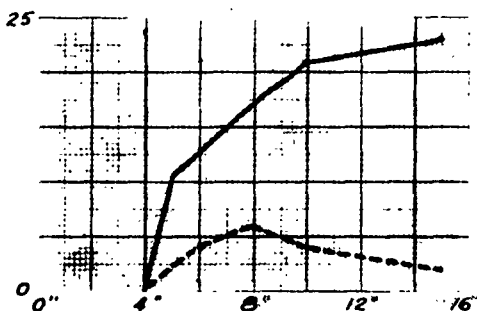
Same composition as 373-D, the barium nitrate being coated with PETN.



R	Z	C	L	H
50	47°	8°	12°	188°
50	48°	7°		354°
50	50°	7°		
50	50°	7°		
50	50°	9°		
50	49°	9°		

375-D

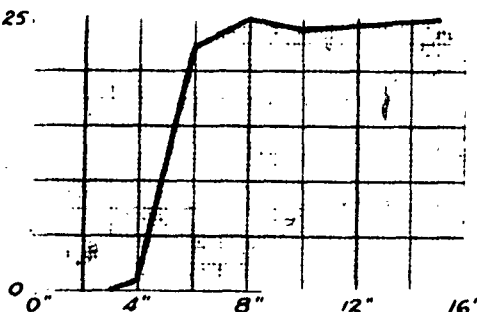
Same composition as 373-D, the barium nitrate being coated with picric acid.



R	Z	C	L	H
50	46°	7°	11°	
50	49°	7°	22°	

384-D

$\text{Hg}(\text{ONC})_2$ 80/- 15%
 Tetracene 100/- 15
 $\text{Ba}(\text{NO}_3)_2$ 200/- 40
 Sb_2S_3 150/200 20
 $\text{Pb}(\text{SCN})_2$ 200/- 5
 TNT 100/- 5

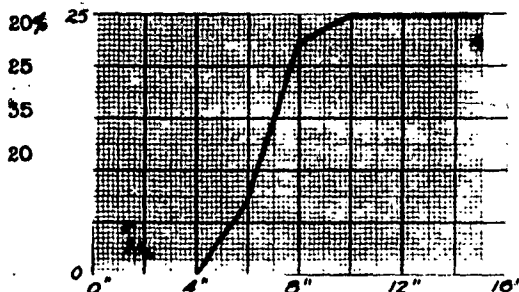


Shots evenly distributed over 360°. No group or zero recorded.

3 misfires

388-D

Hg(ONC)₂ 80/-
Pb styphnate 80/-
Ba(NO₃)₂ 150/200
Sb₂S₃ 200/-



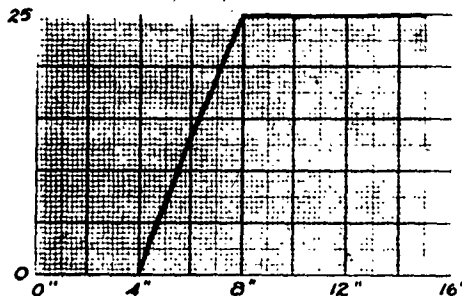
R	Z	G	L	H
100	45°	10°	-	-
100	45°	12°	-	-

1 misfire; primer burned but did not ignite charge.

10 pierced primers.

388-W

Same composition as 388-D

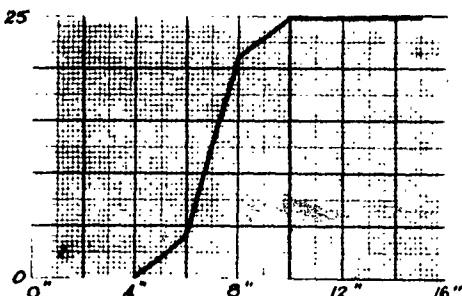


R	Z	G	L	H
50	45°	17°	-	290°

13 misfires; primers burned but did not ignite charge. Test discontinued.

376-D

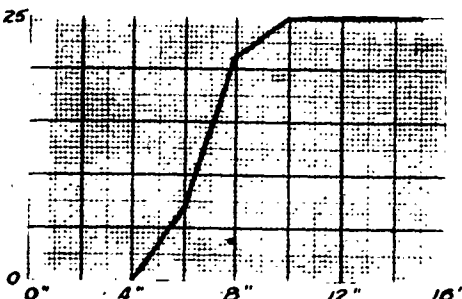
Hg(ONC)₂ 80/-
Pb picrate 150/-
Ba(NO₃)₂ 150/200
Sb₂S₃ 200/-



R	Z	G	L	H
100	47°	10°	11°	292°
100	50°	8°	14°	63°

376-W

Same composition as 376-D



R	Z	G	L	H
100	48°	22°	27°	154°
			42°	171°
			55°	260°
			97°	277°

5 misfires.

On examining the sensitivity curves, 353-3-D appears to be the most satisfactory. It is quite remarkable that barium nitrate of 150/200 mesh and antimony sulfide of 200/- mesh should be the best granulations to use in this type of mixture. When the granulation of either of these ingredients is changed, the sensitivity is appreciably lowered. The least sensitive combination is 353-5-D, where both are 200/- mesh. Lot 353-3-D also gave the most satisfactory hangfire test, although a slight tendency to lag still exists.

7. Varying the Ratio Between Lead Sulfocyanide and Antimony Sulfide

In the basic 353-D mixture, the antimony sulfide, lead sulfocyanide, and T.N.T. are commonly regarded as fuels, although some question might be raised as to the exact function of T.N.T. It is reasonable, however, to view these materials as being consumed in the atmosphere of oxygen which the barium nitrate is supposed to provide. It is, therefore, quite probable that they will not be of equal value as fuels, but that one of them will be more effective than the others.

In order to investigate this point, a mixture was prepared, 378-D, which was practically equivalent to 353-D minus the lead sulfocyanide. A glance at Figure 6 shows that the sensitivity has suffered a marked drop, and that the hangfire test is still very poor.

These results indicated that lead sulfocyanide may be of considerable importance as a fuel. The proportion of lead sulfocyanide was, therefore, increased in 381-D, 381-W, 382-A, and 382-W. The granulation of the barium nitrate and antimony sulfide was altered in these mixtures to conform with 353-3-D, in view of the findings reported above concerning the optimum granulation for these ingredients. Obviously, the mixtures 381-D and 382-D must be compared with 353-3-D, and in order to compare the wet mixtures 381-W and 382-W with 353-3-D, this composition was loaded wet, giving 353-3-W. In figures 7 and 8 will be found these six lots, three wet and three dry, showing the effect of increasing the lead sulfocyanide from 5% to 10% and 15%, the antimony sulfide being decreased correspondingly.

In 353-3 and 381, the wet mixtures are somewhat more sensitive than the dry mixtures, but in 382 both wet and dry mixtures are equally sensitive. By comparing the number of squibs, lags, and hangfires from these six lots, an interesting point can be made.

353-D

Hg(ONC) ₂	80/-	30%
Ba(NO ₃) ₂	200/-	40
Sb ₂ S ₃	150/200	20
Pb(SCN) ₂	200/-	5
TNT	100/-	5

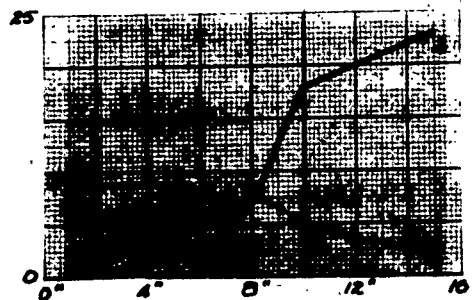


R	Z	G	L	H
75	46°	5°	8°	139°
50	49°	8°	13°	
50	49°	9°	39°	

1 misfire.

378-D

Hg(ONC) ₂	80/-	30%
Ba(NO ₃) ₂	200/-	40
Sb ₂ S ₃	150/200	25
TNT	100/-	5

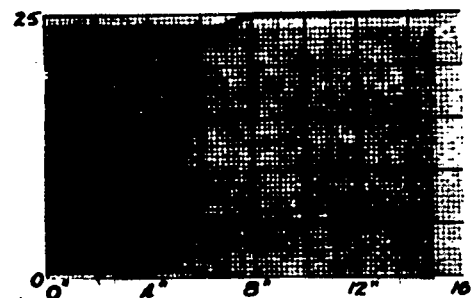


R	Z	G	L	H
100	47°	9°	14°	150°
100	47°	7°	15°	208°
				310°

2 misfires

353-3-W

Hg(ONC) ₂	80/-	30%
Ba(NO ₃) ₂	150/200	40
Sb ₂ S ₃	200/-	20
Pb(SCN) ₂	200/-	5
TNT	100/-	5

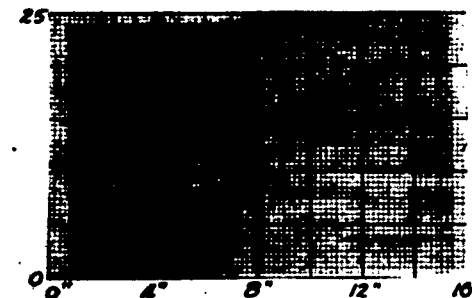


R	Z	G	L	H
100	40°	13°	20°	178°
100	42°	15°	25°	225°
100	45°	20°	25°	
100	50°	27°	52°	
			67°	
			29°	
			60°	
			20°	
			25°	

3 misfires;
primers burned but did
not ignite charge.

391-W

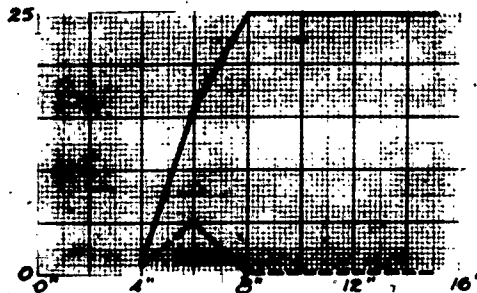
Hg(ONC) ₂	80/-	30%
Ba(NO ₃) ₂	150/200	40
Sb ₂ S ₃	200/-	10
Pb(SCN) ₂	200/-	5
TNT	200/-	10
TNT	100/-	5



R	Z	G	L	H
100	43°	12°	21°	-
100	42°	12°	29°	-

353-3-D

Hg(ONC) ₂	80/-	30%
Ba(NO ₃) ₂	150/200	40
Sb ₂ S ₃	200/-	20
Pb(SCN) ₂	200/-	5
TNT	100/-	5



R	Z	G	L	H
50	50	5	38	-
50	50	9	-	-
100	42	10	-	-

Same composition as
353-3-D

353-3-W

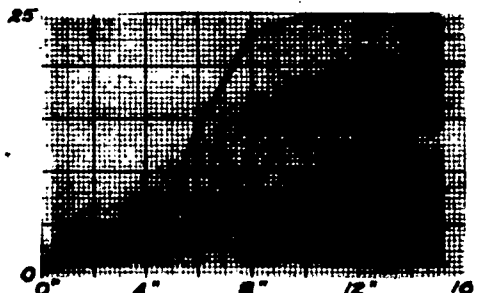


R	Z	G	L	H
100	40	15	20	178
100	42	15	25	228
100	45	20	25	-
100	50	27	32	-
			37	-
			29	-
			60	-
			20	-
			25	-

3 misfires;
primers burned but did
not ignite charge.

381-D

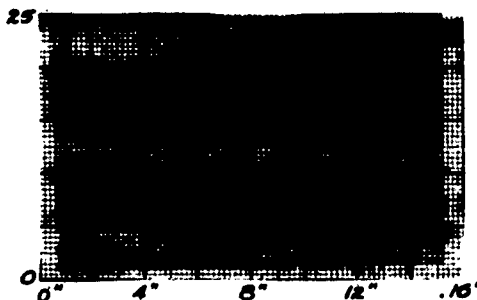
Hg(ONC) ₂	80/-	30%
Ba(NO ₃) ₂	150/200	40
Sb ₂ S ₃	200/-	15
Pb(SCN) ₂	200/-	10
TNT	100/-	5



R	Z	G	L	H
100	41	9	11	-
100	44	7	-	-

381-W

Same composition as
381-D



R	Z	G	L	H
100	45	15	-	-
100	45	15	-	-

Table 1.

<u>% Pb(SCN)₂</u>	<u>No. Squibs</u>		<u>No. Hangfires and Lags</u>	
	<u>Wet</u>	<u>Dry</u>	<u>Wet</u>	<u>Dry</u>
5	0	6	11	1
10	0	0	0	1
15	0	3	1	4

It is plainly seen from Table 1 that the functioning of the wet mixtures is improved by increasing the amount of sulfocyanide present, while the dry mixtures tend to grow worse. This is an interesting result for which no explanation has been found.

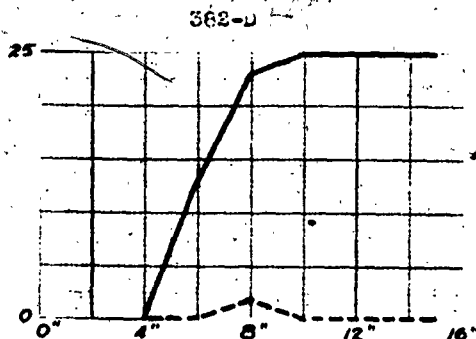
Some doubt began to be felt at this time about the actual value of antimony sulfide in this type of primer. So another composition was loaded, both wet and dry, containing no antimony at all. The T.N.T. was also omitted, since previous experiments had shown it to tend to desensitize this type of priming composition. The fulminate was maintained at 30%, and an approximate oxygen balance was held between the barium nitrate and lead sulfocyanide. The mixtures are 396-D and 396-W.

The results in Figure 8 show a striking difference between the wet and dry mixtures. The hangfire test on 396-D was discontinued after 75 rounds, since no zero or group could be recorded. One lag at 28" was recorded for 396-W. The lower sensitivity of 396-W at 10" and 15" may be discounted, for an excessive amount of gum had been used in mixing, and the pellets were unusually hard.

The results from this series of priming mixtures seemed to indicate that fulminate compositions of high sulfocyanide content could be easily sensitized merely by wet mixing. It was, therefore, decided to try some compositions containing less mercury fulminate. Mixture 389 was prepared with 20% fulminate, the ratio between barium nitrate and lead sulfocyanide being adjusted for oxygen balance. This composition, when loaded wet and dry, showed in even more marked degree the sensitizing effect of wet mixing. Figure 9 shows the results for 389-W and 389-D. No lags or hangfires were obtained with 389-W. It should be noted, however, that one squib was produced in the drop test at 8", indicating that the lower limit for mercury fulminate content had probably been reached.

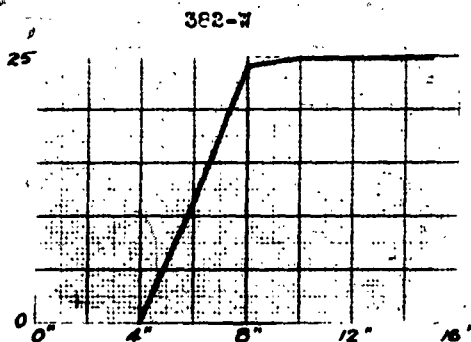
In order to obtain a series of priming compositions showing fully the effect of varying the quantity of mercury ful-

$\text{Hg}(\text{ONC})_2$ 80/- 30%
 $\text{Ba}(\text{NO}_3)_2$ 150/200 40
 Sb_2S_3 200/- 10
 $\text{Pb}(\text{SCN})_2$ 200/- 15
 TNT 100/- 5



R	Z	C	L	H
100	46°	10°	14°	192°
100	44°	10°	17°	194°

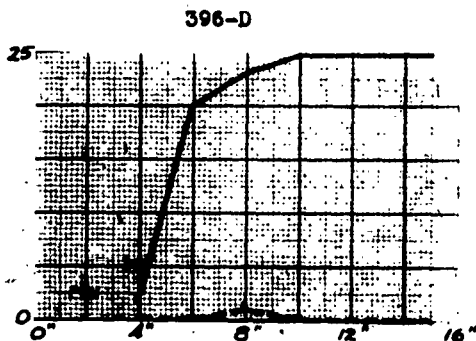
Same composition as 362-D



R	Z	C	L	H
100	45°	10°	-	315°
100	45°	10°	-	-

18 leaky primers.

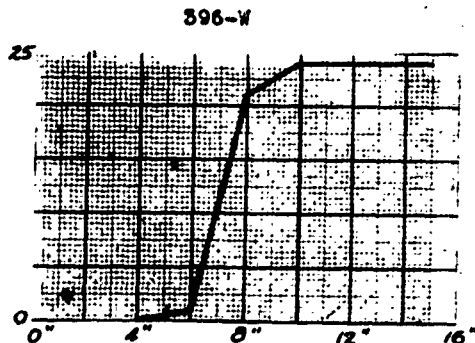
$\text{Hg}(\text{ONC})_2$ 80/- 30%
 $\text{Ba}(\text{NO}_3)_2$ 200/- 41.6
 $\text{Pb}(\text{SCN})_2$ 200/- 28.4



Shots evenly distributed over 360°. No group or zero recorded.

10 misfires.

Same composition as 396-D



R	Z	C	L	H
100	45°	13°	28°	-
100	45°	14°	-	-

minate present, two more mixtures were prepared, 401-W, with 15% fulminate, and 402-W, with 25% fulminate. These were not loaded dry, since the difference between dry and wet loading for this type of composition had been well demonstrated, and it was known that dry loading would only result in squibs and hangfires. It appears immediately from Figure 9 that 15% mercury fulminate is entirely too low, and that 20% is, as surmised, the lower limit for this ingredient. On the other hand, the 25% fulminate mixture (402-W) functioned better than either the 20% (389-W) or the 30% (396-W) mixture (Figures 8 and 9). The group and the zero of the 25% mixture are somewhat smaller than the group and zero of the 20% and 30% mixtures. Furthermore, 402-W shows no squibs and no lags or hangfires. Evidently, this type of three-component mixture functions best with 20% - 25% mercury fulminate. Its functioning at this point is comparable with that of the standard F.A. 70.

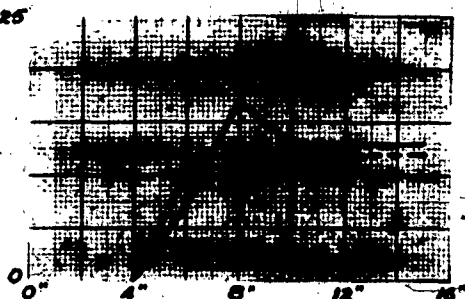
8. Zirconium Mixtures

During recent months the use of metallic zirconium in priming compositions has been given serious consideration. This metal is now available in a finely powdered form in tonnage lots, and at least one loading company has made extensive experiments with it. Accordingly, the investigation of this material as a priming ingredient was begun at Frankford Arsenal, and the results on sixteen compositions are given below.

Previous experiments have shown that the 353-3-W composition is progressively improved by the substitution of lead sulfocyanide for antimony sulfide. The same procedure was applied in testing zirconium, the first mixture prepared was equivalent to 353-3-W with half the antimony sulfide replaced by zirconium. This mixture is known as 391-W, and the results are given in Figure 6 in comparison with 353-3-W. A marked rise in the sensitivity curve can be seen as well as a decrease in the number of lags and hangfires.

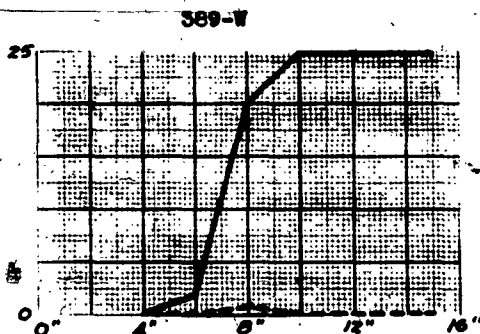
A series of mixtures was next prepared in which the zirconium was progressively increased, and the antimony sulfide entirely eliminated. The mercury fulminate was maintained at 20%, and the barium nitrate and lead sulfocyanide were adjusted to give an oxygen balance with the zirconium. Complete details of the results will be found in Figures 9, 10, and 11, but Table 2 will be found more convenient for comparing the results of the hangfire tests.

$\text{Hg}(\text{ONC})_2$ 80/- 20.4
 $\text{Ba}(\text{NO}_3)_2$ 200/- 47.5
 $\text{Pb}(\text{SCN})_2$ 200/- 32.5



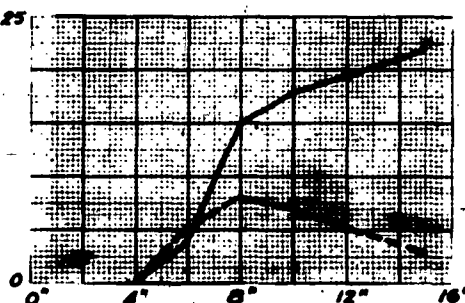
No hangfire test.

Same composition as 389-D



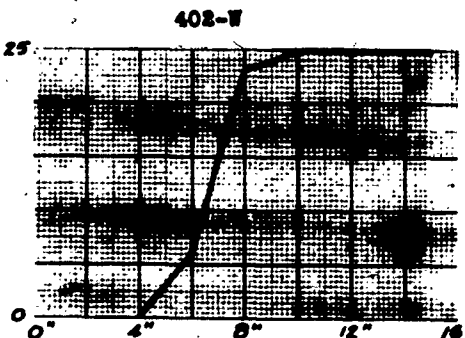
R	Z	G	L	H
100	45°	10°	-	-
100	47°	11°	-	-

$\text{Hg}(\text{ONC})_2$ 80/- 15.4
 $\text{Ba}(\text{NO}_3)_2$ 200/- 50.4
 $\text{Pb}(\text{SCN})_2$ 200/- 34.6



No hangfire test.

$\text{Hg}(\text{ONC})_2$ 80/- 25.4
 $\text{Ba}(\text{NO}_3)_2$ 200/- 44.5
 $\text{Pb}(\text{SCN})_2$ 200/- 30.5



R	Z	G	L	H
75	45°	10°	-	-
75	45°	7°	-	-

393-D

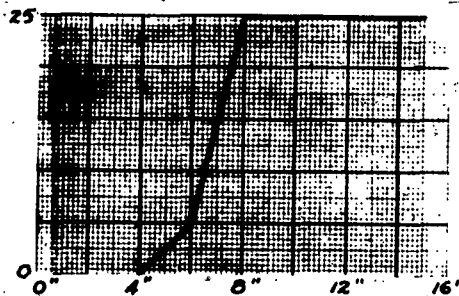
$\text{Hg}(\text{ONC})_2$	80/-	20 %
$\text{Ba}(\text{NO}_3)_2$	200/-	45.9
$\text{Pb}(\text{SCN})_2$	200/-	29.1
Zr	200/-	5



No hangfire test.

393-W

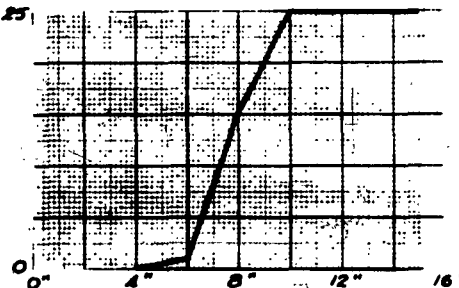
Same composition as 393-D.



R	Z	G	L	H
100	45°	15°	-	-
100	45°	10°	-	-

403-W

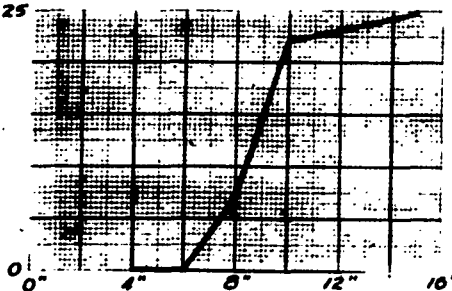
$\text{Hg}(\text{ONC})_2$	80/-	20 %
$\text{Ba}(\text{NO}_3)_2$	200/-	45.4
$\text{Pb}(\text{SCN})_2$	200/-	24.6
Zr	200/-	10



R	Z	G	L	H
75	42°	8°	-	-
75	42°	6°	-	-

404-W

$\text{Hg}(\text{ONC})_2$	80/-	20 %
$\text{Ba}(\text{NO}_3)_2$	200/-	45
$\text{Pb}(\text{SCN})_2$	200/-	20
Zr	200/-	15

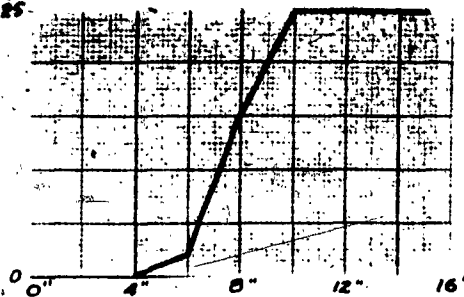


R	Z	G	L	H
75	42°	10°	-	-
75	45°	4°	-	-

38 leaky primers.

394-W

$\text{Hg}(\text{ONO})_2$	50/-	20
$\text{Ba}(\text{NO}_3)_2$	200/-	44.5
$\text{Pb}(\text{SCK})_2$	200/-	15.5
Zr	200/-	20

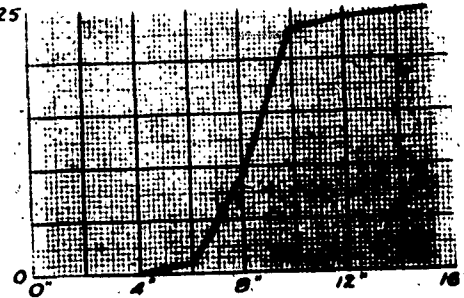


R	Z	G	L	H
100	42°	6°	-	-
100	42°	6°	-	-

5 leaky primers.

408-W

$\text{Hg}(\text{ONO})_2$	50/-	20
$\text{Ba}(\text{NO}_3)_2$	200/-	44
$\text{Pb}(\text{SCK})_2$	200/-	11
Zr	200/-	25

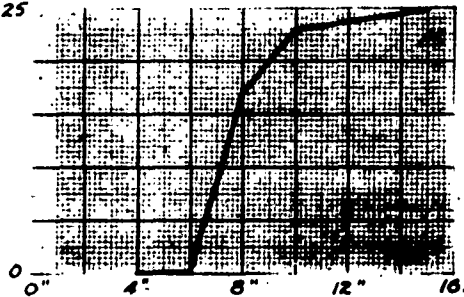


R	Z	G	L	H
75	45°	6°	-	-
43	45°	5°	-	-

6 leaky primers.

395-W

$\text{Hg}(\text{ONO})_2$	50/-	20
$\text{Ba}(\text{NO}_3)_2$	200/-	43.5
$\text{Pb}(\text{SCK})_2$	200/-	6.5
Zr	200/-	20

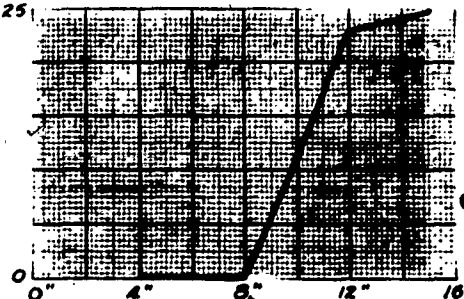


R	Z	G	L	H
100	42°	8°	-	-
100	40°	10°	-	-

8 leaky primers.

407-W

$\text{Hg}(\text{ONO})_2$	50/-	20
$\text{Ba}(\text{NO}_3)_2$	200/-	42.8
Zr	200/-	37.2



R	Z	G	L	H
75	45°	9°	-	-
49	45°	8°	-	-

10 leaky primers.

FIGURE 11

Table 2.

Hg(ONC)₂ 80/- = 20%

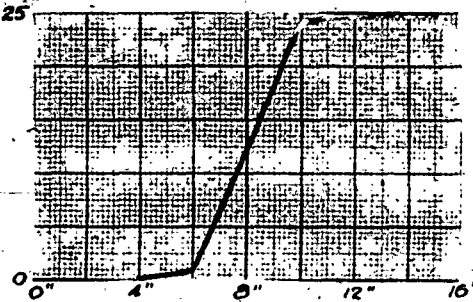
<u>Zr.</u> <u>(%)</u>	<u>Pv(SCN)₂</u> <u>(%)</u>	<u>Lot No.</u>	<u>Rds.</u> <u>Fired</u>	<u>Zero</u>	<u>Group</u>	<u>Lags</u>	<u>Hangfires</u>
0	32.5	389-W	100 100	45° 47°	10° 11°	none "	none "
5	29.1	393-W	100 100	45° 45°	15° 10°	" "	" "
10	24.6	403-W	75 75	42° 42°	8° 8°	" "	" "
15	20.0	404-W	75 75	42° 45°	10° 4°	" "	" "
20	15.5	394-W	100 100	42° 42°	6° 6°	" "	" "
25	11.0	408-W	75 43	45° 45°	6° 5°	" "	" "
30	6.5	395-W	100 100	42° 40°	8° 10°	" "	" "
37.2	0.0	407-W	75 49	45° 45°	9° 8°	" "	" "

The functioning of these mixtures is similar to the functioning of 389-W, the basic composition for this series (see Figure 9). A noticeable narrowing of the group occurs as the zirconium reaches 10%, but at 30% and 37.2% somewhat broader groups can be observed. However, this effect is not conclusive, and too much importance should not be attached to it. The sensitivity shows a general tendency to decrease as the zirconium content increases, although this may be due to the extreme fineness of the zirconium powder. It is interesting to note in Figure 10 that an attempt to load the 5% zirconium mixture dry (393-D) was quite unsuccessful. The sensitizing effect of wet loading is very apparent in this type of mixture.

The 10% and 20% zirconium mixtures were used in another series of tests to determine whether the amount of mercury fulminate used could be changed with advantage. The results obtained by varying the fulminate from 15% to 25% on the 10% and 20% zirconium mixtures are given in Figures 10, 11, 12, and 13. The results of the hangfire tests are tabulated in Table 3.

409-W

$\text{Hg}(\text{ONC})_2$	80/-	15 %
$\text{Ba}(\text{NO}_3)_2$	200/-	49.1
$\text{Pb}(\text{SCN})_2$	200/-	25.9
Zr	200/-	10

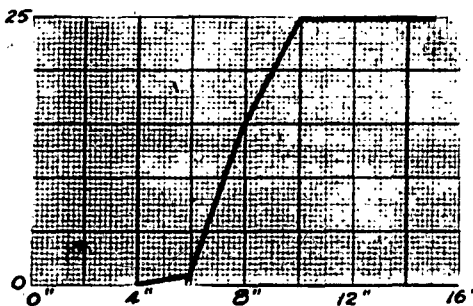


R	2	G	2
75	47°	6°	-
48	47°	7°	-

2 leaky primers.

403-W

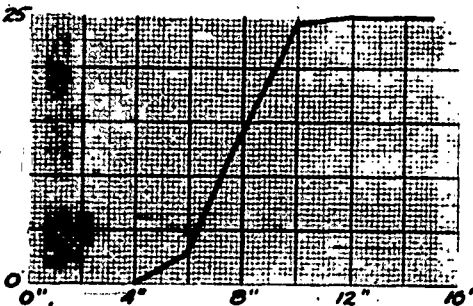
$\text{Hg}(\text{ONC})_2$	80/-	20 %
$\text{Ba}(\text{NO}_3)_2$	200/-	45.4
$\text{Pb}(\text{SCN})_2$	200/-	24.6
Zr	200/-	10



R	Z	G	L	H
75	42°	8°	-	-
75	42°	8°	-	-

410-W

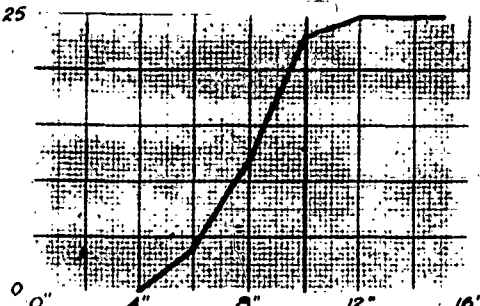
$\text{Hg}(\text{ONC})_2$	80/-	25 %
$\text{Ba}(\text{NO}_3)_2$	200/-	42.5
$\text{Pb}(\text{SCN})_2$	200/-	22.5
Zr	200/-	10



R	Z	G	L	H
75	45°	8°	-	-
49	45°	9°	-	-

411-W

$\text{Hg}(\text{ONC})_2$	80/-	15%
$\text{Ba}(\text{NO}_3)_2$	200/-	47.8
$\text{Pb}(\text{SCN})_2$	200/-	17.2
Zr	200/-	20



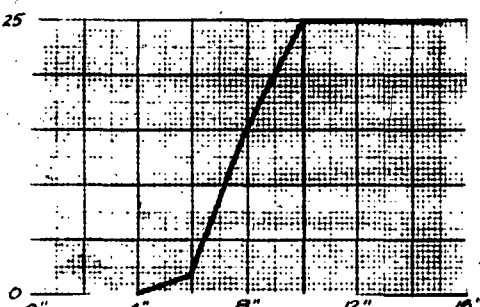
R	Z	G	L	H
75	42°	15°	90°	260°
75	42°	14°	30°	300°
75	48°	11°	16°	
75	49°	13°		

1 misfire; primer burned but did not ignite charge.

1 leaky primer.
2 pierced primers.

394-W

$\text{Hg}(\text{ONC})_2$	80/-	20%
$\text{Ba}(\text{NO}_3)_2$	200/-	44.5
$\text{Pb}(\text{SCN})_2$	200/-	15.5
Zr	200/-	20

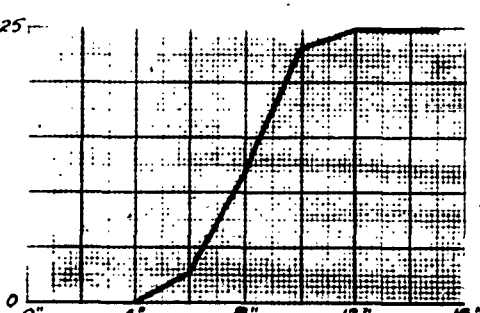


R	Z	G	L	H
100	42°	6°	-	-
100	42°	6°	-	-

5 leaky primers.

412-W

$\text{Hg}(\text{ONC})_2$	80/-	25%
$\text{Ba}(\text{NO}_3)_2$	200/-	41.5
$\text{Pb}(\text{SCN})_2$	200/-	13.5
Zr	200/-	20



R	Z	G	L	H
75	40°	13°	19°	355°
75	42°	13°	23°	
75	48°	10°		
75	48°	10°		

8 leaky primers.
13 pierced primers.

Table 3.

Zirconium = 10%

$H_2(ONC)_2$	Lot No.	Rds. Fired	Zero	Group	Lags	Hangfires
15	409-W	75	47°	6°	none	none
		48	47°	7°	"	"
20	403-W	75	42°	8°	"	"
		75	42°	8°	"	"
25	410-W	75	45°	8°	"	"
		49	45°	9°	"	"

Zirconium = 20%

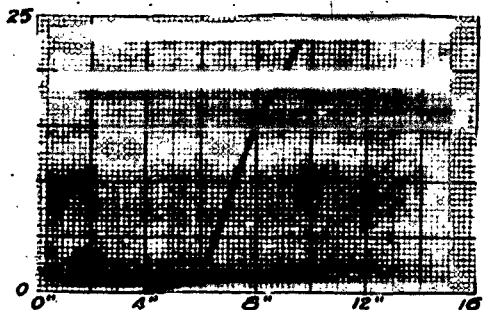
15	411-W	75	42°	15°	90°	280°
		75	42°	14°	30°	300°
		75	48°	11°	16°	
		75	49°	13°		
20	394-W	100	42°	6°	none	none
		100	42°	6°	"	"
25	412-W	75	40°	13°	19°	
		75	42°	13°		
		75	48°	10°	23°	335°
		75	48°	10°		

Apparently the 10% zirconium mixture is unaffected by relatively wide changes in the fulminate content. On the other hand, lags and hangfires are very conspicuous when the fulminate is increased or decreased in the 20% zirconium mixture. The indications are that in this type of composition the best performance corresponds to a certain critical "concentration" of fulminate, and that functioning is seriously impaired by increasing or decreasing this concentration.

The effect of changing the granulation of the barium nitrate in zirconium mixtures was investigated for 403-W and 394-W. Lots 419-W and 420-W were prepared identical in composition with 403-W, except that 150/200 and 100/150 barium nitrate was used, respectively. The results in Figure 14 show that barium nitrate coarser than 200/- cannot be used in 403-W. Similarly, a mixture known as 421-W was prepared identical with 394-W, except that 150/200 barium nitrate was used. Again, the results in Figure 15 show that very fine barium nitrate is

403-U

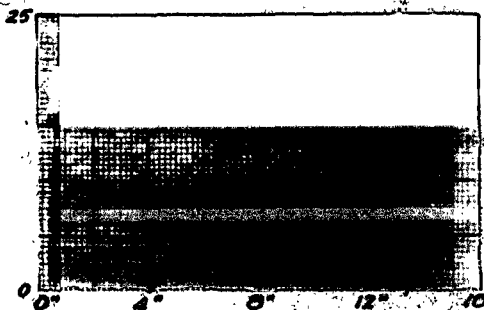
Hg(ONC)₂ 80/- 20.3
 Cu(NO₃)₂ 200/- 45.4
 Pb(SCN)₂ 200/- 24.6
 Zn 200/- 10



R	Z	G	L	H
75	42°	8°	-	-
75	42°	8°	-	-

419-U

Same composition as
 403-U, except that
 100/200 mesh barium
 nitrate was used.

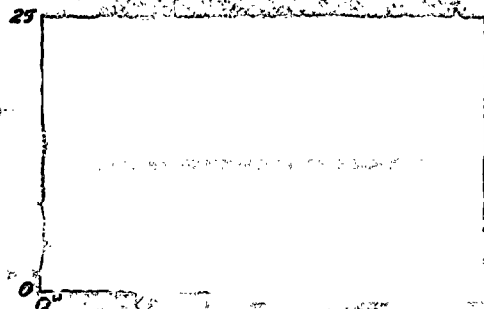


R	Z	G	L	H
75	42°	13°	18°	20°
75	42°	13°	20°	25°

4 misfire.

420-U

Same composition as
 403-U, except that
 100/200 mesh barium
 nitrate was used.

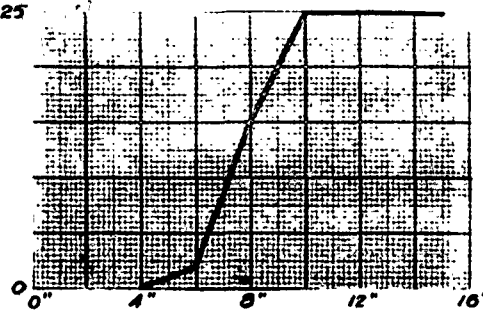


R	Z	G	L	H
75	42°	21°	25°	28°
75	42°	21°	25°	28°

4 misfire.
 4 misfire.
 burning device.

394-W

Hg(ONC) ₂	E0/-	20 %
Ba(NO ₃) ₂	E50/-	44.5
Pb(SCH) ₂	E00/-	15.5
Kr	E00/-	20

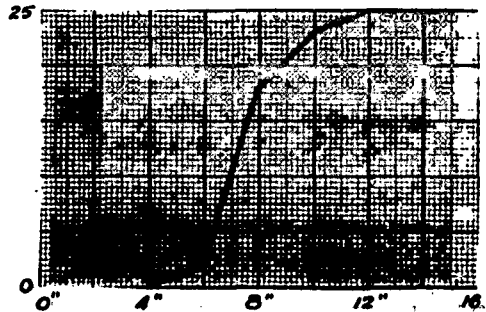


R	Z	C	L	H
100	42°	6°	-	-
100	42°	6°	-	-

5 leaky primers.

421-W

Same composition as
394-W, except that
100% barium
nitrate was used.



R	Z	C	L	H
75	42°	15°	20°	-
75	42°	13°	78°	-

5 misfires.

necessary for this type of composition.

It is interesting to note that the sensitivity curves for these three mixtures show them to be somewhat more sensitive than their parent mixtures at 6" and 8"; but at 10" two of the mixtures (420-W and 421-W) are less sensitive than the parent mixtures. As a matter of fact, all three mixtures were less sensitive than their parent mixtures under full machine gun action, for in the hangfire test four misfires were recorded for 419-W and 420-W and five misfires for 421-W.

The tendency toward leaky primers is characteristic of zirconium mixtures containing more than 10% of this metal. This is a serious defect which would have to be eliminated before this type of mixture could be considered for service ammunition.

9. Varying the Granulation of the Mercury Fulminate

It has been known for some time that coarse mercury fulminate is more sensitive to impact than fine fulminate (6). This, of course, applies only to the pure material. To determine whether the same rule applies to mercury fulminate priming mixtures, it was decided to load 353-3 both wet and dry with 150/- fulminate instead of the 80/- material. The resulting two mixtures are known as 353-6-D and 353-6-W, and the data obtained with them are given in Figure 16 in comparison with 353-3-D and 353-3-W.

The sensitivity of the wet mixture of 150/- mesh fulminate shows a slight increase at 4", although this is not necessarily significant. The squibs obtained with the dry 80/- mesh mercury fulminate mixture show up again in the dry 150/- mesh fulminate mixture. Furthermore, the sensitivity of the dry mixture of 150/- mesh fulminate has dropped to a very marked degree at 6" and 8". The hangfire tests show that both 150/- mesh mixtures are distinctly inferior to their parent mixtures.

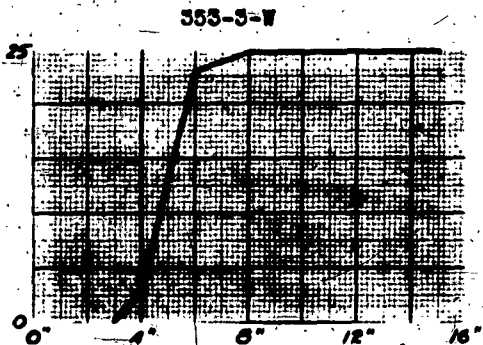
The next experiments along this line were made on 401-W, 389-W, and 402-W which represent, in the order given, a mercury fulminate content of 15%, 20%, and 25%, 80/- material being used on all three. Six new compositions were prepared by using 80/150 and 150/- fulminate in each of these three mixtures in place of the 80/- material. The relation between these six lots and the three parent mixtures from which they derived is shown in Table 4.

$\text{Hg}(\text{ONC})_2$ 80/- 30 % 25
 $\text{Ba}(\text{NO}_3)_2$ 150/200 40
 $\text{Pb}(\text{SCH})_2$ 200/- 5
 Sb_2S_3 200/- 20
 TNF 100/- 5



R	Z	C	L	H
50	50°	5°	38°	
50	50°	9°		
100	42°	10°		

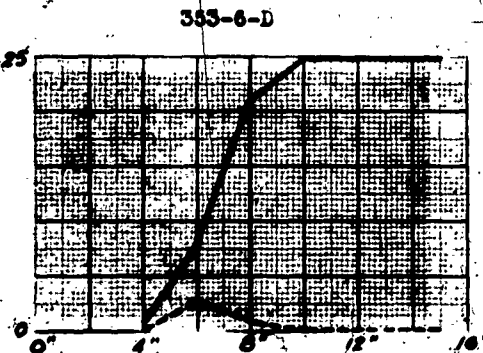
Same composition as 353-3-D



R	Z	C	L	H
100	40°	15°	20°	17°
100	42°	15°	25°	20°
100	45°	20°	25°	20°
100	50°	27°	32°	25°
			37°	
			39°	
			60°	
			80°	
			85°	

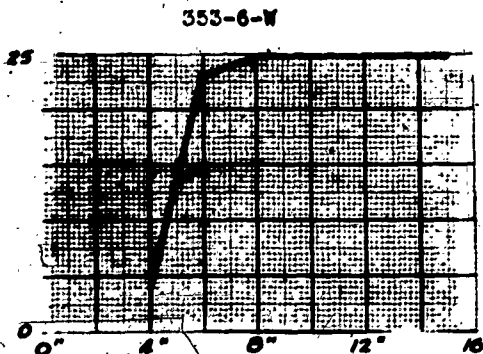
3 misfires; primers burned but did not ignite charge.

Same composition as 353-5-D, except that 150/- mesh mercury fulminate was used.



R	Z	C	L	H
100	47°	6°	15°	24°
92	45°	6°	15°	

Same composition as 353-5-D, except that 150/- mesh mercury fulminate was used.



R	Z	C	L	H
100	48°	20°	14°	14°
20	50°	15°	18°	14°
			56°	20°
			79°	20°
			80°	20°
			80°	20°

43 misfires.

Table 4.

Granulation of Fulminate

<u>Fulminate (%)</u>	<u>80/-</u>	<u>80/150</u>	<u>150/-</u>
15	401-W	413-W	414-W
20	389-W	415-W	416-W
25	402-W	417-W	418-W

The results given in Figures 17, 18, and 19 show clearly that the sensitivity of the 15% and 20% fulminate compositions is very much lower when either fine or coarse fulminate is used exclusively. In the drop test, 413-W and 414-W produced more squibs than fired primers. Lots 415-W and 416-W were also very poor in the drop test when compared with 389-W. The general performance improves, however, as the mercury fulminate is increased, and in 417-W and 418-W the drop test was considered good enough to warrant a hangfire test. But even 417-W and 418-W showed a somewhat lower sensitivity than 402-W, from which they were derived.

The hangfire results on 417-W and 418-W are unfavorable, whereas the parent mixture, 402-W, functioned satisfactorily.

It will be noted that the proportions of barium nitrate and lead sulfocyanide used in 413-W, 414-W, 415-W, and 416-W are not quite the same as in 401-W and 389-W, with which they have been compared. This is due to an error in weighing, but it is not considered serious enough to invalidate the comparison or the conclusions to be drawn from the results.

Potassium Chlorate Compositions

1. Pretreatment of Potassium Chlorate

Experiments on the pretreatment or activation of barium nitrate in fulminate compositions have already been described. The same kind of experiment was made on the F.A. 70 composition, in which the potassium chlorate was washed with 0.2% KNO_3 in acetone and then dried on the water bath. This mixture is known as 370-W, the results of which appear in Figure 20 in comparison with F.A. 70.

The sensitivity of 370-W appears to have dropped slightly at 10". Otherwise, very little effect can be noted. The somewhat smaller group and lower zero of 370-W are not decisive, since the group for F.A. 70 may vary from 4° to 7° and the zero from 44° to 47°.

Unless otherwise indicated, the granulation of in-

gradients in chlorate compositions is the same as required by specifications for the F.A.70 composition, listed on Page 31.

2. Tetracene Mixtures

Tetracene was used as a sensitizer in two chlorate mixtures, with and without T.N.T. The results are given in Figure 20 under 356-W and 357-W.

As shown by 357-W, tetracene cannot be used as a substitute for T.N.T. in chlorate mixtures. The sensitivity curve shows a marked drop at 10", while the hangfire test is unaffected. For 356-W, where both T.N.T. and tetracene were used, there is no noticeable change in either drop test or hangfire test.

Two additional mixtures were prepared containing 10% and 15% tetracene, but it was found impossible to rub them into the charging plates properly. Tetracene is an extremely fine, bulky material, and the mixtures formed a mush when moistened with gum solution. Experiments with tetracene in the F.A. 70 mixture have been abandoned.

3. Varying the Granulation of the Potassium Chlorate and Antimony Sulfide

Specifications for the F.A.70 priming composition require that the sieve fractions for each ingredient shall be as follows:

Potassium Chlorate.

Through 80 mesh sieve,-	At least	99%
" 150 " " -	Approximately	50%
" 200 " " -	Not more than	20%

Antimony Sulfide:

Through 100 mesh, on 150 mesh,-	33.3%
" 150 " " 200 " -	33.3%
" 200 " -----	33.3%

Lead Sulfoeyanide.

Through 150 mesh sieve,-	100%
" 200 " " " -	at least 95%

Trinitrotoluol (T.N.T.):

Through 100 mesh sieve,-	100%
--------------------------	------

401-W

 $\text{Hg}(\text{ONC})_2$ 80/-

15 % 25

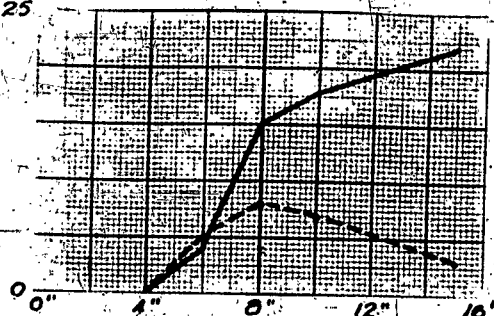
 $\text{Ba}(\text{NO}_3)_2$ 200/-

50.4

 $\text{Pb}(\text{SCN})_2$ 200/-

34.6

No hangfire test.



413-W

 $\text{Hg}(\text{ONC})_2$ 80/150

15 % 25

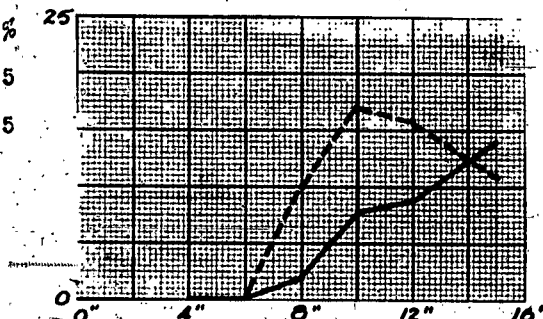
 $\text{Ba}(\text{NO}_3)_2$ 200/-

45.5

 $\text{Pb}(\text{SCN})_2$ 200/-

39.5

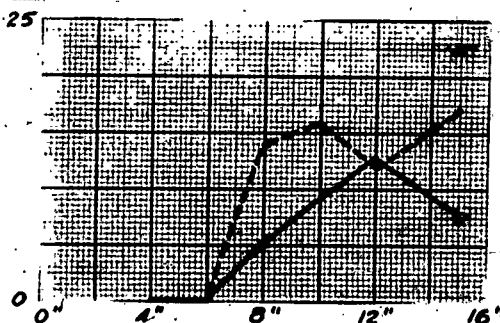
No hangfire test.



414-W

Same composition as
413-W, except that
150/- mesh mercury
fulminate was used.

No hangfire test.



389-W

200/-

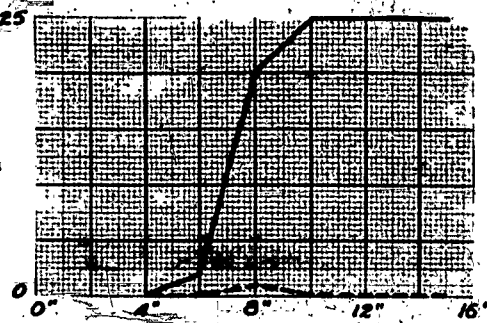
20 %

200/-

47.5

200/-

32.5



R	Z	G	L	M
100	45°	10°	-	-
100	47°	11°	-	-

415-W

200/150

20 %

200/-

42.8

200/-

37.2



No hangfire test.

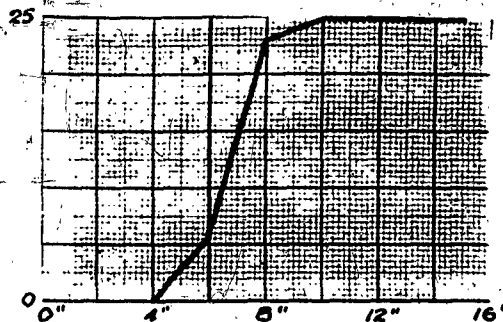
416-W

Resolution as
except that
mercury
was used.



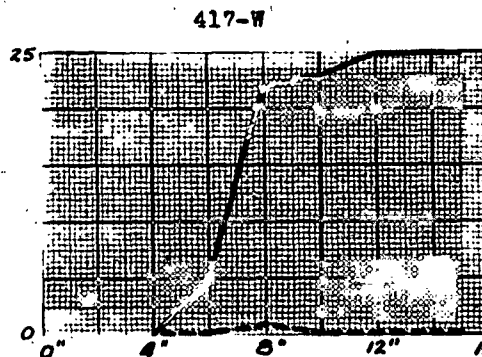
No hangfire test.

Hg(ONC)₂ 80/- 25 %
 Ba(NO₃)₂ 200/- 44.5
 Pb(SCN)₂ 200/- 30.5



R	Z	G	L	H
75	43°	10°	-	-
75	45°	7°	-	-

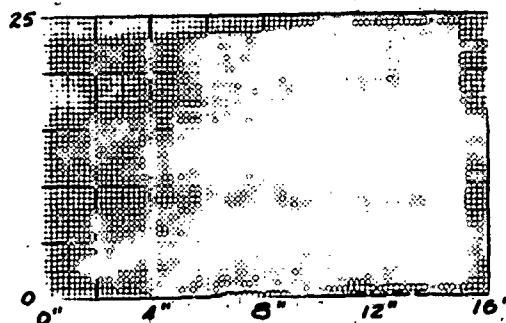
Same composition as 402-W, except that 80/150 mesh mercury fulminate was used.



R	Z	G	L	H
75	45°	15°	33°	380°
75	47°	17°	-	-

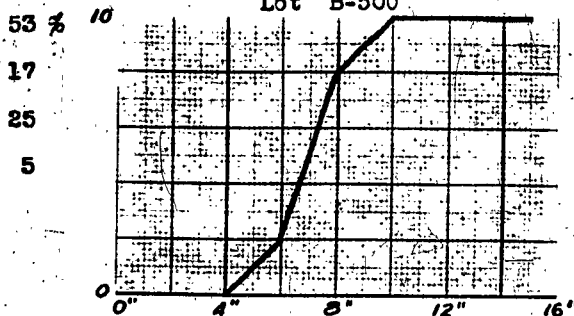
2 misfires; primers burned but did not ignite charge.

Same composition as 402-W, except that 150/- mesh mercury fulminate was used.



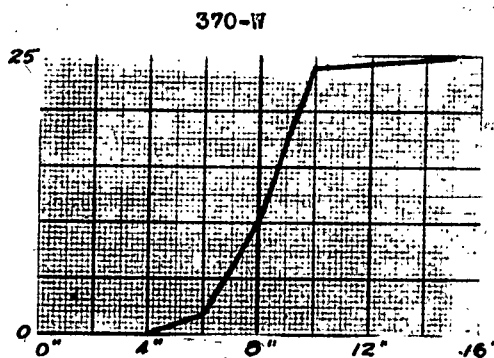
R	Z	G	L
75	48°	13°	-
75	48°	15°	-

KClO₃
 Sb₂S₃
 Pb(SCN)₂
 TNT



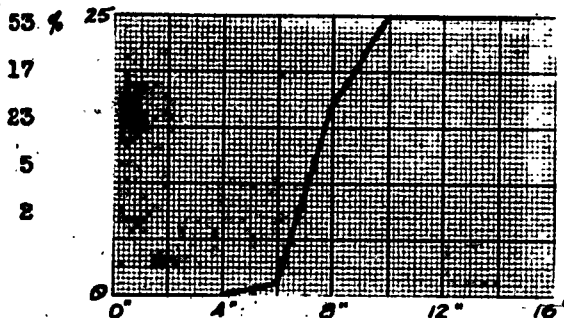
R	Z	G	L	H
75	42°	6°	-	-
75	42°	5°	-	-
75	42°	5°	-	-
75	42°	6°	-	-

the composition as
 F. A. 70, the potassium
 nitrate being coated
 with KNO₃.



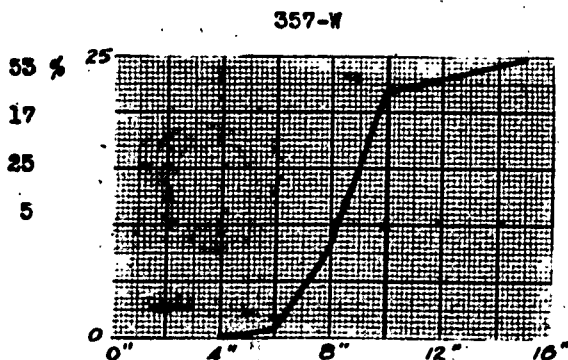
R	Z	G	L	H
50	44°	4°	-	-
50	44°	5°	-	-

KClO₃
 Sb₂S₃
 Pb(SCN)₂
 TNT
 Tetraene



R	Z	G	L	H
50	46°	4°	-	-
50	46°	4°	-	-

KClO₃
 Sb₂S₃
 Pb(SCN)₂
 Tetraene



R	Z	G	L	H
50	45°	4°	-	-
50	44°	5°	-	-

According to these requirements, some variation is allowed in the sieve fractions 150/200 and 200/- for the potassium chlorate. To determine the effect such a variation might have on the functioning of the primer, nine mixtures were prepared. The granulation of both potassium chlorate and antimony sulfide were varied through three sieve fractions: 100/150, 150/200, and 200/-, all nine of the possible combinations being used. The granulation of the lead sulfocyanide and T.N.T. was constant and the composition of the mixture was equivalent to the F.A.70. Turning to Figures 21, 22, and 23, Lots 379-W to 379-9-W, it will be seen that it is difficult to draw any definite conclusions from either the drop-test or the hangfire test. The slight differences shown by the nine mixtures are no greater than the variations encountered in daily production where the granulations are comparatively constant. In the drop list, all nine mixtures fired at 10" and failed at 4". In the hangfire tests, the groups varied from 4° to 8° and the zeros from 42° to 48°.

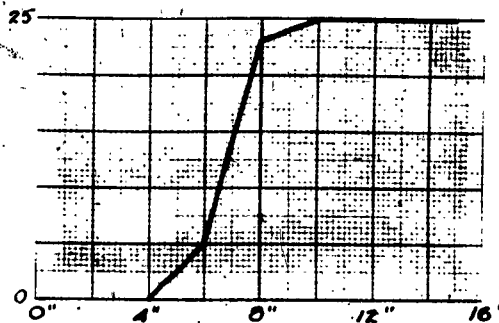
This is a remarkable result in view of the wide range in the granulations. However, in the light of some later experiments, the explanation is quite simple. These experiments to be described later, indicate that **ignition in** the F.A. 70 composition begins between the potassium chlorate and lead sulfocyanide. The flame from these two ingredients spreads rapidly through the pellet, and it is only in the later stages of combustion that the antimony sulfide becomes involved. Thus the granulation of the antimony sulfide can hardly influence the functioning of the primer to any great extent, within a reasonable range of granulation. The potassium chlorate, on the other hand, dissolves in the gum solution, and when the mixture is finally dried, the chlorate crystallizes out in the form of exceedingly fine crystals. The result of this is that each particle of material in the pellet is encased in a film of dry gum containing fine crystals of chlorate. It is plain then, that the granulation of the chlorate in contact with the lead sulfocyanide is fairly constant, no matter how the granulation is chosen before mixing. Therefore, in all of the nine mixtures prepared, the granulations of the two materials which largely govern sensitivity and speed of combustion were not varied at all. The constancy of the results confirms this view.

Some interesting results were obtained by varying the granulations of the potassium chlorate and antimony sulfide in dry mixtures of the F.A. 70. It is plain that the results given in Figure 23, Lots 380-D, 380-2-D, and 380-3-D, show, the effects of dry loading rather than the effects of changes in granulation. Lags and hangfires are much in evidence and the groups have broadened considerably. The ballistic excellence of the F.A. 70 is evidently dependent upon wet loading.

379-1

KClO₃ 100/150
 Sb₂S₃ 100/150
 Pb(SCN)₂
 TNT

53 %
 17
 25
 5

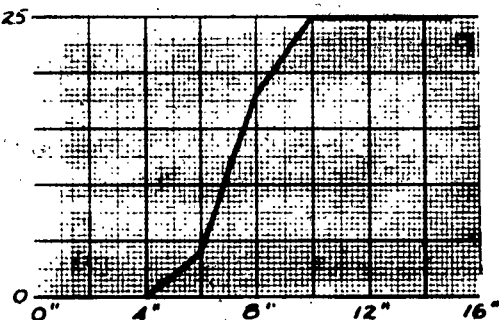


R	Z	C	L	H
100	43°	4°	-	-
100	42°	6°	-	-

379-2-W

KClO₃ 100/150
 Sb₂S₃ 150/200
 Pb(SCN)₂
 TNT

53 %
 17
 25
 5

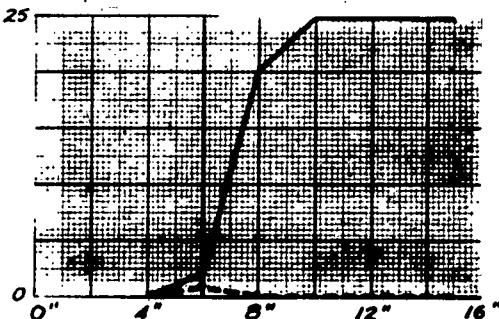


R	Z	C	L	H
100	44°	5°	-	-
100	44°	6°	-	-

379-3-W

KClO₃ 100/150
 Sb₂S₃ 200/-
 Pb(SCN)₂
 TNT

53 %
 17
 25
 5

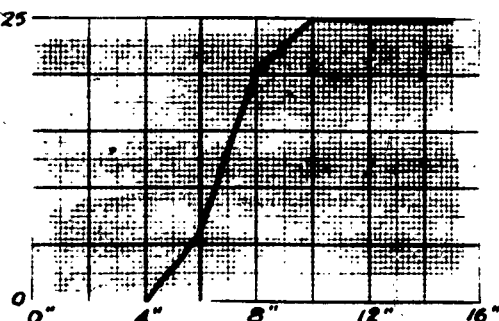


R	Z	C	L	H
100	46°	6°	-	-
100	47°	5°	-	-

379-4-W

KClO₃ 150/200
 Sb₂S₃ 100/150
 Pb(SCN)₂
 TNT

53 %
 17
 25
 5



R	Z	C	L	H
100	44°	7°	-	-
100	44°	8°	-	-

FIGURE 21

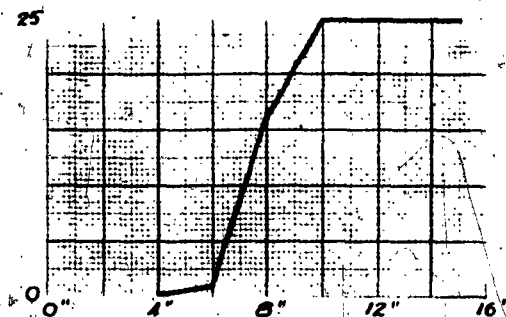
HClO_3 150/200

Sn_2S_3 150/200

$\text{Pb}(\text{SCN})_2$

TNT

53 %
17
25
5



R	Z	C	L	H
100	45°	5°	-	-
100	43°	8°	-	-

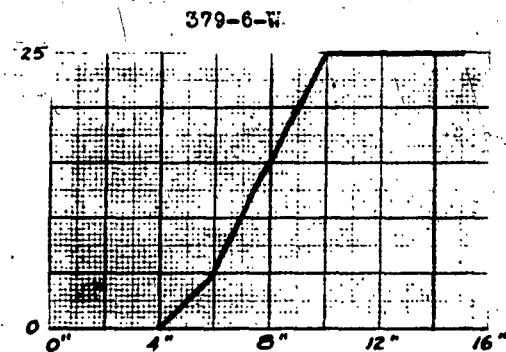
HClO_3 150/200

Sn_2S_3 200/-

$\text{Pb}(\text{SCN})_2$

TNT

53 %
17
25
5



R	Z	C	L	H
100	44°	6°	-	-
100	45°	5°	-	-

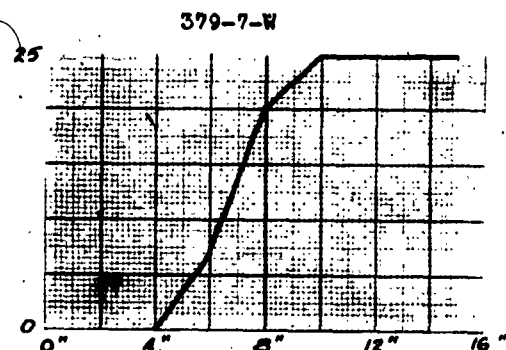
HClO_3 200/-

Sn_2S_3 100/150

$\text{Pb}(\text{SCN})_2$

TNT

53 %
17
25
5



R	Z	C	L	H
100	48°	5°	-	-
100	46°	5°	-	-

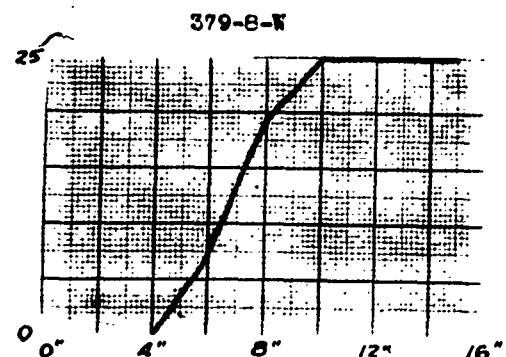
HClO_3 200/-

Sn_2S_3 150/200

$\text{Pb}(\text{SCN})_2$

TNT

53 %
17
25
5



R	Z	C	L	H
100	46°	5°	-	-
100	45°	5°	-	-

379-9-W

KC10₃ 200/-

53 %

Sb₂S₃ 200/-

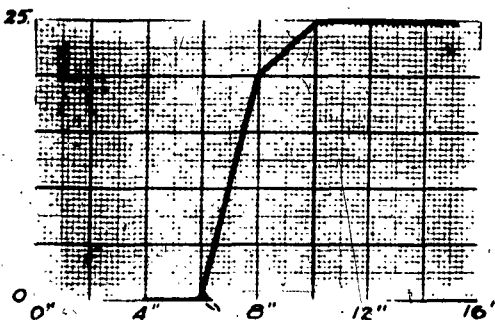
17

Pb(SCN)₂

25

TNT

5



R	Z	G	L	H
100	45°	6°	-	-
100	46°	5°	-	-

380-D

KC10₃ 150/200

53 %

Sb₂S₃ 150/200

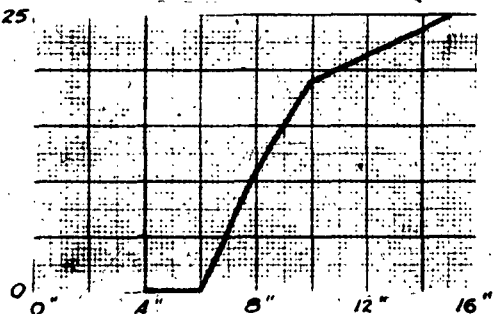
17

Pb(SCN)₂

25

TNT

5



R	Z	G	L	H
100	41°	8°	-	190°
100	41°	11°	-	-

380-2-D

KC10₃ 150/200

53 %

Sb₂S₃ 200/-

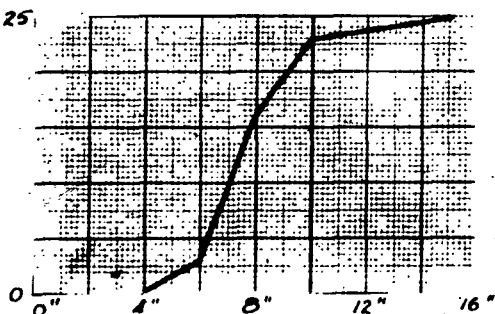
17

Pb(SCN)₂

25

TNT

5



R	Z	G	L	H
100	43°	5°	10°	-
50	45°	9°	-	-

380-3-D

KC10₃ 200/-

53 %

Sb₂S₃ 150/200

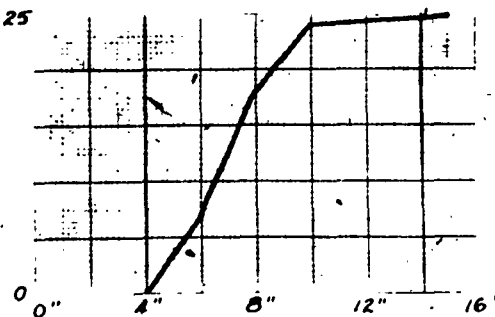
17

Pb(SCN)₂

25

TNT

5



R	Z	G	L	H
100	41°	8°	92°	115°
21	43°	11°	-	-

4. The Relative Importance of Antimony Sulfide and Lead Sulfocyanide in the F.A. 70 Mixture

The interesting results obtained by eliminating antimony sulfide from mercury fulminate compositions led to some similar experiments with the F.A. 70 composition. Mixtures 397-W and 397-2-W contain only potassium chlorate, lead sulfocyanide, and T.N.T. The chlorate in 397-W is finer than in 397-2-W, and contrary to the results obtained with the 397 series of mixtures, a definite drop in sensitivity at 10" and 8" occurs in the mixture containing the coarser chlorate. The results are given in Figure 24.

Two additional mixtures were prepared without T.N.T., containing only potassium chlorate and lead sulfocyanide. Fine chlorate was used in 398-W, and somewhat coarser chlorate in 398-2-W. Again, a drop in sensitivity at 10" and 8" occurs in the mixture containing the coarser chlorate (Figure 24). The sensitizing effect of T.N.T. on potassium chlorate is at once apparent on comparing 398-W with 397-W and 398-2-W with 397-2-W.

The groups from the hangfire test on 398-W are somewhat broad, but otherwise the functioning is good on all four of these mixtures from which the antimony sulfide has been eliminated. The hangfire tests on 397-W, 397-2-W, and 398-2-W are quite as good as the hangfire tests on F.A. 70 from daily production.

So far, experiments with both chlorate primers and fulminate primers indicate that lead sulfocyanide is of greater value as a fuel than antimony sulfide. In order to test this idea further, two additional mixtures were prepared, 405-W containing potassium chlorate, antimony sulfide, and T.N.T., and 406-W containing only potassium chlorate and antimony sulfide. It can be judged from Figure 25 how very insensitive these compositions are. But even in these mixtures, the marked sensitizing effect of T.N.T. on potassium chlorate is apparent. It should be noted that 406-W is very nearly the same as the primitive mixture used by Dreyse a hundred years ago.

The unimportance of antimony sulfide as a fuel was indicated several years ago by the experiments of A. S. Cushman (8) in which it was found that lead and iron sulfides could be successfully substituted for stibnite. However, the full meaning of this highly suggestive result escaped notice, and little effort has been made to use a definite chemical compound in place of the mineral of uncertain properties.

397-W

KClO₃ 150/200
" 200/-

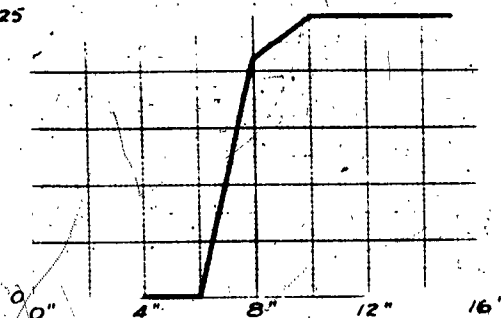
25.3%
25.3

Pb(SCN)₂

44.4

TNT

5.0



R	Z	G	L	H
100	40°	7°	-	-
100	42°	7°	-	-

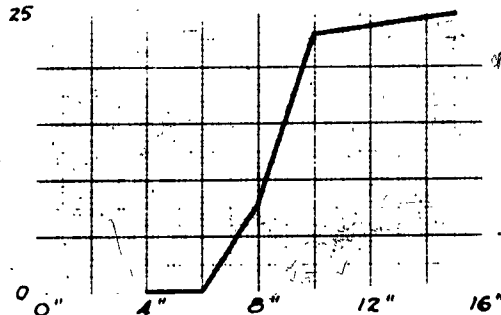
398-W

KClO₃ 150/200
" 200/-

26.7%
26.7

Pb(SCN)₂

46.6



R	Z	G	L	H
100	42°	9°	-	-
100	42°	11°	-	-

397-Z-W

KClO₃ 150/200

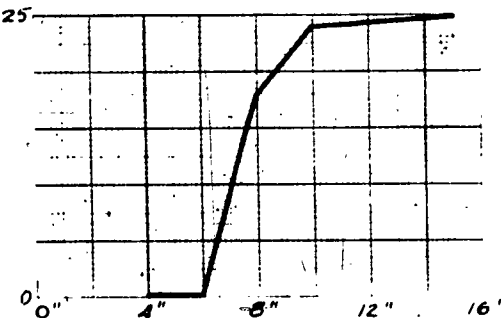
50.6%

Pb(SCN)₂

44.4

TNT

5.0



R	Z	G	L	H
75	45°	6°	-	-
75	45°	6°	-	-

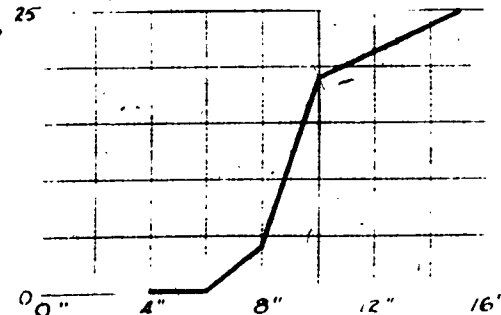
398-Z-W

KClO₃ 150/200

53.4%

Pb(SCN)₂

40.0



R	Z	G	L	H
75	45°	7°	-	-
75	45°	8°	-	-

405-W

KClO₃ 150/200

49.35

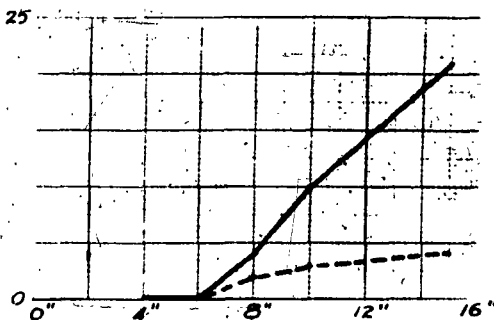
Sb₂S₃ 200/-

45.7

TNT

5.0

No hangfire test



406-W

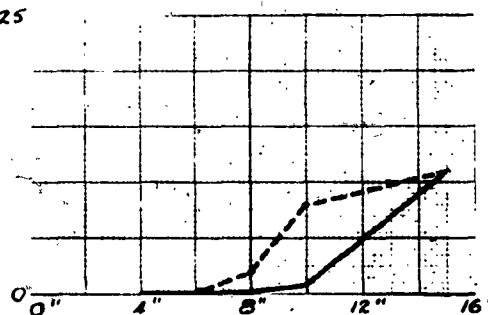
KClO₃ 150/200

52 %

Sb₂S₃ 200/-

48

No hangfire test



399-W

Diazol 80/-

15 %

Ba(NO₃)₂ 200/-

52.9

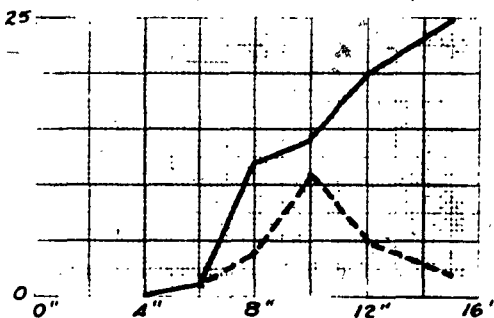
Pb(SCN)₂ 200/-

27.1

Zr 200/-

5.0

No hangfire test



400-W

Diazol 80/-

25 %

Ba(NO₃)₂ 200/-

48.9

Pb(SCN)₂ 200/-

21.1

Zr 200/-

5.0

R	Z	G	L	H
100	45°	16°	41°	-
100	42°	20°		

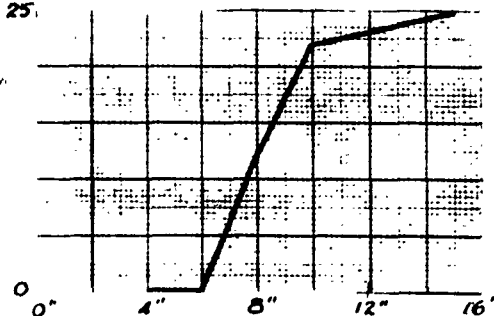


FIGURE 25

Noncorrosive Non-fulminate Compositions

1. Rathsburg Composition

The Rathsburg patents mentioned previously (3) have recently revived interest in noncorrosive compositions containing no mercury fulminate. These compositions depend principally on the normal lead salt of trinitroresorcinal, or styphnic acid for their effectiveness, and it is specified that tetracene (guanylnitrosaminoguanyl tetracene) be used in small quantities to sensitize the mixtures properly. Lead styphnate is relatively insensitive when used in ordinary proportions (30% to 40%) in barium nitrate mixtures.

It has been shown that tetracene is not an initiator in priming compositions in the sense that mercury fulminate is an initiator. It has also been shown that tetracene will not sensitize potassium chlorate compositions in the way T.N.T. sensitizes them. It was, therefore, considered desirable to examine the properties of tetracene in lead styphnate mixtures. The lead styphnate used in the experiments was furnished by the Remington Arms Co. Apparently, it had been prepared from magnesium styphnate and lead nitrate, as it had the characteristic brown, sandy appearance which this method of preparation gives it. Two mixtures were prepared after the formula given in the Rathsburg patent, in one of which the tetracene had been omitted. Each of these was loaded both wet and dry, so that a total of four compositions were studied. Figure 26 shows the results from 386-W and 386-D (with tetracene) and 387-W and 387-D (without tetracene.).

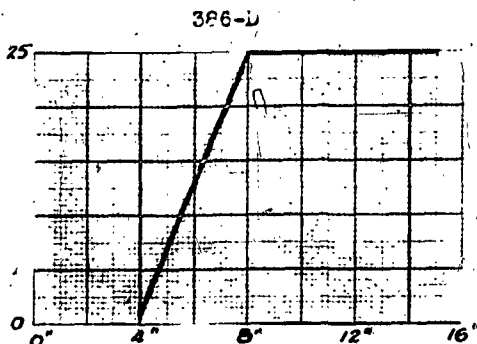
The remarkable effect of only 3% tetracene is at once evident. The mixtures without tetracene were so insensitive, the hangfire test was omitted. The deleterious effect of wet loading on lead styphnate mixtures is again apparent in both 386 and 387. This effect had been observed previously in fulminate mixtures containing lead styphnate (see 386-D and 386-W, Fig. 4).

The similarity between lead styphnate and lead picrate suggested that the latter compound might serve in this type of composition. Accordingly, lots 386 and 387 were duplicated using basic lead picrate in place of lead styphnate. These mixtures were also loaded wet and dry. As shown in Figure 27, 360-W and 360-D were prepared with 3% tetracene, and 363-W and 363-D contained no tetracene.

The sensitizing action of tetracene is again very pronounced. Furthermore, the desensitizing effect of wet loading

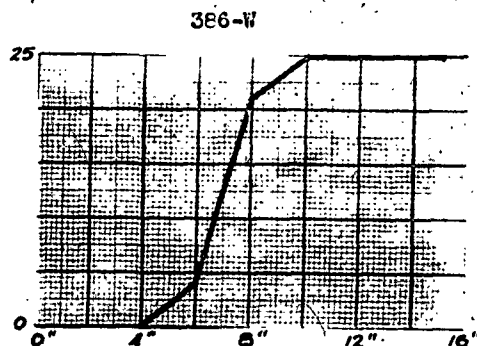
Pb styphnate 80/-
 $\text{Ba}(\text{NO}_3)_2$ 150/200
 Sb_2S_3 150/200
 CaSi_2 200/-
 FeO_2 200/-
 Tetracene 100/-

38 %
 38
 5
 11
 5
 3



R	Z	G	L	H
190	42°	7°	-	-
90	42°	10°	-	-

Same composition as
 386-D

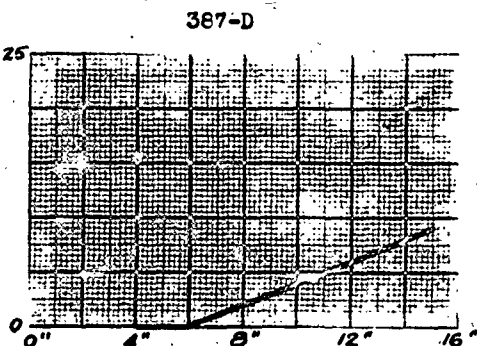


R	Z	G	L	H
100	45°	10°	19°	-
100	44°	10°	-	-

1 misfire

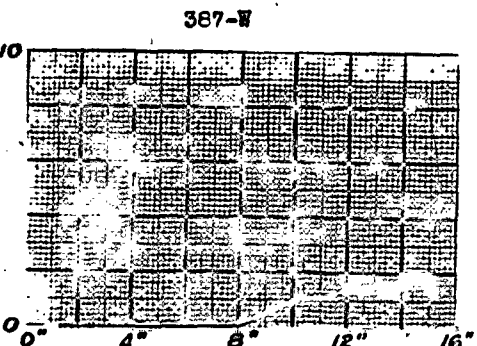
Pb styphnate 80/-
 $\text{Ba}(\text{NO}_3)_2$ 150/200
 Sb_2S_3 150/200
 CaSi_2 200/-
 FeO_2 200/-

38 %
 38
 6
 12
 6



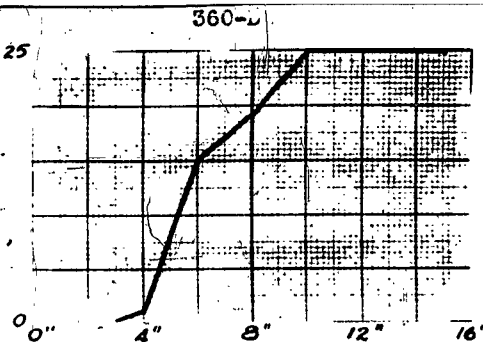
No hangfire test.

Same composition as
 387-D



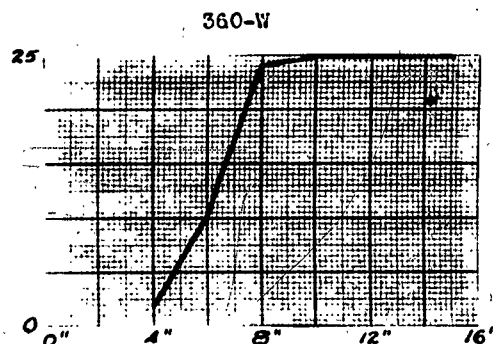
No hangfire test.

Pb picrate 150/- 38 %
 $\text{Ba}(\text{NO}_3)_2$ 150/200 38
 Sb_2S_3 150/200 5
 CaSi_2 200/- 11
 PbO_2 200/- 5
 Tetracene 100/- 3



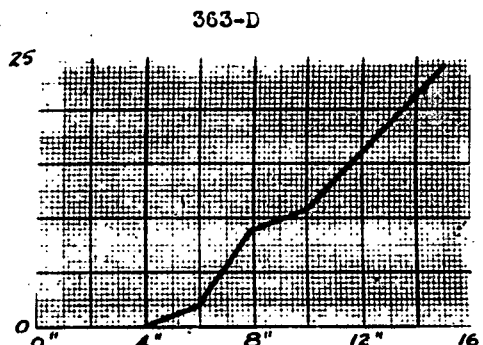
R	Z	G	L	H
50	46°	14°	26°	161°
50	45°	16°	52°	274°
			90°	285°

Same composition as
 360-D



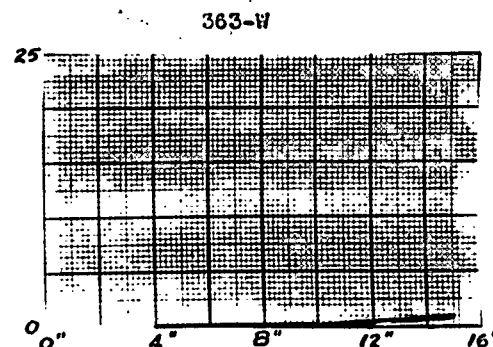
R	Z	G	L	H
100	42°	16°	25°	143°
100	43°	15°	100°	240°

Pb picrate 150/- 38 %
 $\text{Ba}(\text{NO}_3)_2$ 150/200 38
 Sb_2S_3 150/200 6
 CaSi_2 200/- 12
 PbO_2 200/- 6



No hangfire test.

Same composition as
 363-D



No hangfire test.

It is not known whether the flame flashing out in all directions from under the anvil point is communicated to the remainder of the pellet or not. It is quite probable that the mechanical force of the flame from under the anvil point merely shatters the rest of the pellet and blows the ingredients out through the flash hole into the cartridge. In this case the individual particles would undoubtedly derive considerable heat from the flame, and might play an important part in igniting the powder charge. At any rate, it is certain that particles of solid or molten material are always ejected by primers, for they can be caught upon microscope slides and examined. The number of particles or droplets and their degree of subdivision vary with different primers, and sometimes in the same primer. These particles may or may not, according to their size, reach the temperature of the hot gases comprising the flame.

The ballistic properties of a given primer will depend ultimately on the number of powder grains ignited by the primer. Experiments with dummy powder show clearly that, in most cases, about one third of all the powder grains in .30 caliber ammunition are ignited directly by the primer. The remaining two thirds of the grains are ignited by the flame from those. It is clear, then, that if a given primer ignites only one sixth of the charge, there will be a greater delay in the combustion of the charge than if one third had been ignited. This is, perhaps, the most plausible explanation of hangfires.

Granulation

It is very necessary to stress the idea that primer flames are the result of rapid burning rather than detonation. Primers that detonate are unserviceable in that the cup is usually blown back against the head of the bolt, and leaks develop around the primer pocket. Hardly any "set-back" can be observed with primers that function properly, and so it is assumed that combustion in this case is considerably slower, approaching the "progressive burning" of smokeless powders. Furthermore, the duration of primer combustion is of the order of 10^{-3} to 10^{-4} seconds, and this certainly rules out detonation phenomena.

Small arms priming compositions are essentially inflammable mixtures sensitive to impact. The chief reaction that occurs in all ordinary primers seems to be oxidation of the "fuels" by the oxidizing salt. The common fuels are antimony sulfide and the sulfocyanides of heavy metals, oxidizing salts include, chiefly, potassium chlorate, barium nitrate, and sometimes peroxides of various metals. From the chemical nature of the oxidizers and fuels, it is apparent, then, that they are in

themselves non-explosive under impact. It is, therefore, reasonable to assume that the sensitivity of a priming composition resides in the interface between the particles of fuel and oxidizer. Combustion of the primer pellet must originate somewhere in the surface separating the fuel and oxidizer. Granting this, it is obvious that the flame must be propagated along this interface as the pellet is consumed, and that the speed of combustion of the pellet may possibly be controlled by regulating the area of contact between fuel and oxidizer.

To clarify this idea still further, it is interesting to consider a mixture of one gram molecule of lead nitrate (oxidizer) and one gram molecule of resorcinol (fuel). The extreme limit of coarseness for a mixture of these materials is represented in Figure 28a by a single crystal of lead nitrate placed against a single crystal of resorcinol. Considering the masses represented in the illustrations, which have been drawn to scale, the area in contact is small. But by cutting each crystal in two, and rearranging as in Figure 28b, the contact area has been trebled. The process of subdivision as shown in Figures 28c and d naturally results in a rapid increase in contact area and a corresponding increase in the rate of reaction between the two substances. Theoretically, the degree of subdivision might extend all the way through the region of colloids into molecular dimensions, where the ultimate of fineness would be reached. As a matter of fact, these regions of fine dispersion are quite attainable, and some very interesting work might be done investigating the properties of priming compositions composed of inorganic colloids. In the case of lead nitrate and resorcinol, the ultimate degree of intimate mixing could be reached, of course, by actually allowing the two to combine under suitable conditions, forming one molecule of lead dinitroresorcinol and eliminating two molecules of water. In this substance, shown structurally in Figure 28e, the oxidizing part of the lead nitrate molecule has actually been attached to the resorcinol ring, and the result is, of course, a highly explosive compound. In doing this, though, the identity of the original ingredients has been lost, and it would be quite incorrect to say that lead dinitroresorcinol is an intimate mixture of lead nitrate and resorcinol. It is instructive, however, to follow the granulation from extreme coarseness to extreme fineness, and to see how the area in contact and the reactivity increase with the degree of subdivision.

It is believed that this accounts in large measure for the many leaky primers caused by certain zirconium mixtures. The zirconium used in these mixtures came in the form of an extraordinarily fine powder, and its speed of combustion when mixed with barium nitrate was very high. However, the fact should not be overlooked that zirconium has a very high heat of combustion,

and this factor probably contributed appreciably to the violence of the zirconium primers.

From the foregoing it is evident that the interfacial area between the two ingredients of a binary mixture will be determined by the surface area of the coarser ingredient, i.e., the ingredient of smaller surface area. If, then, the granulation of the oxidizer is given, there is no need to grind the fuel finer than that granulation giving the same surface area as the oxidizer. The rate of combustion will increase up to the point where the fuel presents the same surface area as the oxidizer, beyond that point continued grinding of the fuel should not affect the rate of combustion. On the other hand, if the fuel is ground very much finer than is necessary for a given fineness of oxidizer, a loss of sensitivity to impact may easily result. By grinding the fuel too fine, some of the fuel crystals will be in contact with each other, the excess surface area of the fuel will be in contact with itself, so to speak. Some of the energy of impact will then be absorbed by the sliding of fuel crystals over each other, and there will be less energy available for the sliding of fuel crystals over oxidizer crystals. Since ignition occurs only in the latter circumstance, it is plain that a loss of sensitivity should result when one of the ingredients is ground too fine. For a given mixture of fuel and oxidizer, then, there is a certain optimum ratio which the particle size of one should bear to the particle size of the other. This ratio can be calculated from the total volumes of the ingredients by letting

V_o = total volume of oxidizer,

V_f = total volume of fuel,

d_o = mean diameter of oxidizer crystals,

d_f = mean diameter of fuel crystals.

If all the oxidizer crystals are of the same size and shape, then,

the volume of each oxidizer crystal = $K_o d_o^3$, and the area of each oxidizer crystal = $k_o d_o^2$, both K_o and k_o depending on the shape of the particle. Therefore, the total surface area of the oxidizer will be

$$S_o = \frac{V_o}{K_o d_o^3} k_o d_o^2 = \frac{k_o V_o}{K_o d_o}$$

In the same way, the area of the fuel will be

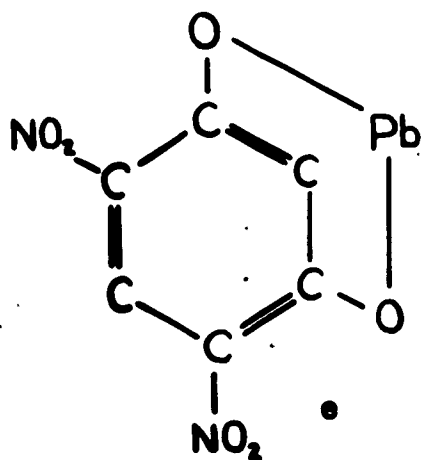
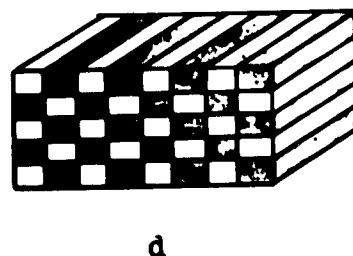
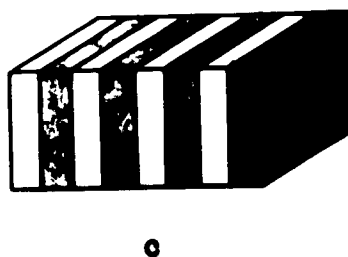
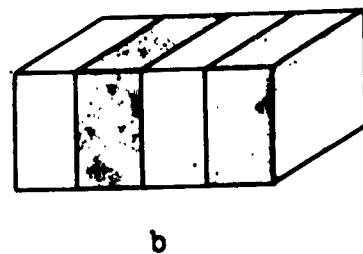
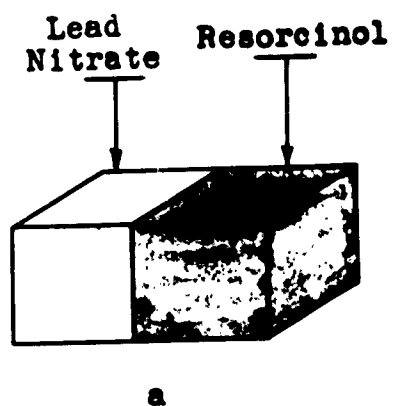


FIGURE 28

$$S_f = \frac{k_f V_f}{K_f d_f}$$

Both K_f and k_f depend on the shape of the particles of fuel, and are not necessarily the same as K_o and k_o .

When the surface areas of oxidizer and fuel are the same,

$$\frac{k_o V_o}{K_o d_o} = \frac{k_f V_f}{K_f d_f}$$

and the ratio of the particle diameters will be

$$\frac{d_o}{d_f} = \frac{K_f k_o V_o}{K_o k_f V_f} \quad \text{----- (1)}$$

Example:

Consider a mixture of 52 gms. potassium chlorate and 48 gms. antimony sulfide. If the particles of both ingredients have the same shape, the constants K_f , K_o , k_f , and k_o cancel, and the particle sizes will be in the same ratio as the volumes of the ingredients. Since the density of potassium chlorate is 2.32 and density of antimony sulfide is 4.65, it follows that

$$\frac{d_o}{d_f} = \frac{(52)(4.65)}{(2.32)(48)} = 2.17$$

In most cases, the particles of priming ingredients do not have the same shape, and the coefficients of Equation 1 do not cancel. It should be noted also that Equation 1 says nothing about the absolute fineness of mixtures, it merely gives the ratio between particle sizes corresponding to maximum sensitivity to impact, whatever the granulation may be. Theoretically, the absolute fineness should affect only the speed of combustion, as shown previously.

Some interesting properties can be deduced from a binary mixture in which the particle size ratio does not satisfy Equation 1. In such a mixture, one of the ingredients has been ground too fine, and its surface is greater than the surface of the other ingredient. Using the same symbols as before, the total surface of the mixture will be

$$A = S_o + S_f$$

Now, if $S_f > S_o$, the amount of fuel surface in contact with oxidizer surface will be equal to the oxidizer surface. Therefore, the total extent of contact between fuel and oxidizer will be equal to $2S_o$. The difference

$$\text{or} \quad \frac{(S_o + S_f) - 2S_o}{S_f - S_o},$$

represents the excess surface of the fuel not in contact with the oxidizer. The fraction of the total surface of the mixture existing as contact surface between fuel and oxidizer can be expressed

$$F = \frac{2S_o}{S_o + S_f} \quad \text{when } S_f > S_o \quad \text{-----}(2)$$

$$\text{or} \quad F = \frac{2S_f}{S_o + S_f} \quad \text{when } S_f < S_o \quad \text{-----}(3)$$

Returning to the mixture in which the fuel was ground too fine, it is seen that Equation 2 applies, since $S_f > S_o$. If now, a coarser granulation of fuel be substituted, S_f will decrease and F will increase until, when $S_f = S_o$, $F = 1$, and optimum ratio will have been reached. If still coarser fuel is now introduced, equation 3 applies, since $S_f < S_o$. The same order of effects might have been obtained had a finer granulation of oxidizer been introduced.

Figure 29 shows graphically the way in which the particle size ratio affects the extent of contact between fuel and oxidizer. Values of F expressed in per cent are used as ordinates, and the ratios of d_o/d_f have been used as abscissae. The optimum value of d_o/d_f for each mixture appears as a maximum in F at which $F = 100\%$ as required by Equation 1. The curve to the left of each maximum represents Equation 2; to the right, Equation 3.

In most priming compositions an approximate "oxygen balance" is maintained between fuels and oxidizers, so that a maximum of heat may be obtained from the limited volume of the primer pellet. It becomes interesting, then, to discover how the optimum value of d_o/d_f varies with different pairs of oxidizers and fuels taken in stoichiometric proportions. Table 5 shows calculated values of particle size ratio when the fuel and oxidizer surfaces in contact are 100% of the total surface.

SURFACE IN CONTACT VS. PARTICLE SIZE RATIO

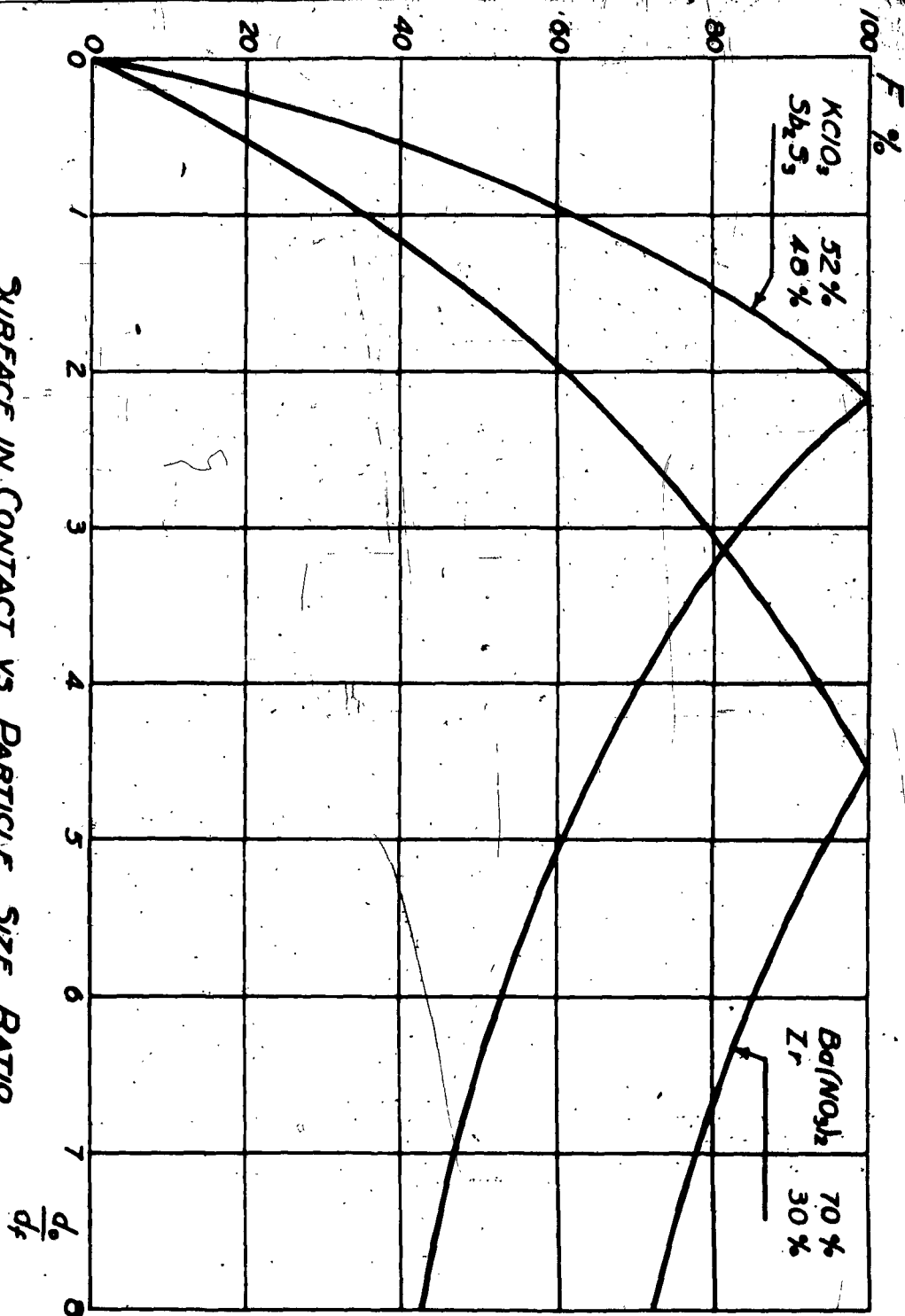


FIGURE 29

Table 5.
Optimum Particle Size Ratios d_o/d_f

	<u>KClO₃</u>	<u>Ba(NO₃)₂</u>	<u>Sr(ClO₃)₂</u>	<u>Pb(NO₃)₂</u>	<u>PbO₂</u>	<u>BaCrO₄</u>
Sb ₂ S ₃	2.17	1.98	1.75	1.80	3.14	4.63
Pb(SCN) ₂	1.87	1.71	1.51	1.55	2.71	4.00
CuSCN	2.06	1.89	1.66	1.71	2.99	4.41
ZnS	2.22	2.03	1.78	1.84	3.21	4.74
S	2.23	2.08	1.83	1.88	3.29	4.85
Zr	2.48	2.26	2.00	2.05	3.59	5.29

The optimum particle size ratios in Table 5 represent thirty-six binary mixtures of oxidizers and fuels, taken in stoichiometric proportions. It will be noted that the values in all cases are greater than one, which means that the oxidizer must be coarser than the fuel for maximum sensitivity. Moreover, the ratios for the commonly used ingredients lie between 1.5 and 2.5, a fairly narrow range. In the case of bulky oxidizers (PbO₂ and BaCrO₄) and dense fuels (Zr), the ratios may increase to 4 or 5.

It is believed that much important work might be done verifying the theory of granulation experimentally. The several mixtures described under Experimental Compositions which were intended to show the effects of changes in granulation were inconclusive, since many disturbing factors were present. What is needed is a determination of speed of combustion and sensitivity to impact of simple binary mixtures. In this connection it is believed that the most fertile field of experimentation would be the region of microscopic powders, i.e., powders finer than 200 mesh. Powders in this region can be accurately separated and graded within quite narrow limits of granulation, using an air separator similar to the one designed by Roller (7). The field of colloidal dimensions also promises to be of interest in primer development. The use of inorganic colloids in priming compositions would transform ignition systems in a very literal sense from the "black powder class" into the "smokeless powder class" of explosives. There is no intention here of barring organic compounds from the scene; their value as substitutes for inorganic salts simply has not materialized.

The gum solution used in wet loading probably plays an important part in altering the granulation of the soluble constituents. The salts dissolved by the gum are deposited as exceedingly fine crystals when the pellet is dried, and these, being in intimate contact with the fuels, must affect the combustion of the pellet to some extent. Strangely enough, the dried gum containing potassium chlorate crystals is very difficult to ignite even with a Bunsen flame. So that the gum itself is of little value as a fuel in starting ignition.

The method used for determining the surface area of powders will be described briefly. It is assumed in all cases that the general shape of the particle is an ellipsoid of three unequal axes, $a > b > c$. When the material is sprinkled on a microscope slide, it is evident that the individual particles will be arranged with their shortest dimension, the c axis, perpendicular to the slide, this being the stable position for an ellipsoid at rest. It is quite simple then to measure the a and b axes with a filar micrometer, since these extend parallel to the plane of the slide. The average volume of the particles is determined by dividing the weight of a known number of them by their density and number. Knowing the volume of each particle, the c axis may then be found, since a and b are known. The surface area is then calculated from a , b , and c .

An experimental method for getting the surface area is also under development. In this method the material is allowed to stand for some time immersed in a liquid in which it is insoluble. The liquid holds in solution a substance capable of reacting with the insoluble material, and after a time the surface of each particle will have reacted sufficiently to give a measurable change in weight of the original sample. This change in weight is proportional to the surface area of the sample. Some success has been had by treating barium nitrate powders in this way with alcoholic solutions containing sulfate ions. A similar technique, making use of adsorption phenomena, has been described by Harkins and Gans (9).

Coefficients of Friction

The ignition of priming mixtures has been assumed to take place through the heat developed by static or kinetic friction between the individual particles. The sensitivity to impact will depend, then, upon two factors:

1. The minimum temperature at which the mixture will ignite.
2. The rate at which heat is developed in the solid interfaces.

if the rate at which heat is developed in the solid interfaces is not great enough, the heat will be conducted away or otherwise dissipated before the interface becomes hot enough to ignite. The rate of heat development is determined, in turn, by the coefficient of friction between the particles. So that the sensitivity is finally proportional to the ignition temperature and to the coefficient of friction means not only that

the rate of heating is greater, but also that the total amount of heat developed in the mixture is greater, and that a large portion of the energy of **impact** appears as heat in the mixture.

If the coefficients of friction of explosives were substantially constant, or were inoperative in any way, it would follow that the sensitivity would be proportional to the ignition temperature only. Taylor and Rinkenbach (10) have shown however, that this is not the case. In their investigation of twenty initiating explosives, no relationship between the two was found. The data given in table 6 are representative of their results.

Table 6

	<u>Ignition Temp. °C.</u>	<u>Sensitivity, cms. (0.5 kgrm. weight)</u>
Silver acetylide D	200	79
Hexamethylene-triperoxide- diamine	200	8
Dulcital hexanitrate	205	47
Mercurous azide	298	6
Lead styphnate	293	50

Evidently, the best way to account for the lack of proportionality is to assign large values of frictional resistance to those compounds of **high sensitivity**. For instance, **mercurous azide** should exhibit a much larger coefficient of friction than lead styphnate. This idea could be checked by measuring the angle of repose of a pile of mercurous azide crystals and comparing with the angle of repose of lead styphnate. Since the tangent of the angle of repose is equal to the coefficient of static friction, a very simple means of checking the theory is available. It should be pointed out, though, that the sensitivity data of Taylor and Rinkenbach was obtained by crushing the samples between hardened steel surfaces, so that the frictional forces determining ignition were probably those between the steel surfaces and the explosive crystals, and not necessarily those between the crystals themselves. It would seem advisable in theoretical investigations to wrap the sample in tin or lead foil, in order that the friction of crystal against crystal might be the sole source of heat (11).

The coefficient of friction between two substances is, of course, a definite property of the substances, and cannot be altered. In a given composition it would seem, then, that there would be little chance of increasing or decreasing sensitivity in this way. However, it does not seem entirely

fantastic to suggest that by making use of adsorption phenomena, some profound changes might be effected in the surface conditions of the ingredients. The net result of such experiments, of course, would be the creation of a new surface having different properties. Every crystal would be sheathed in a molecular envelope too small to affect burning properties, yet thick enough to offer increased resistance to sliding motion. As a matter of fact, this has already been done in a rather crude way by adding powdered glass to priming mixtures. If the glass is fine enough, it will adhere to the coarser particles by adsorption and endow them, in effect, with a higher coefficient of friction. In recent years, the silicides of calcium and iron have been used with success in place of glass, and the tendency is to regard them not only as abrasives, but as fuels as well. The common assumption that stibnite also has abrasive properties is open to question. The hardness of stibnite is only 2; it is, therefore, about as soft as gypsum, and even softer than the finger nail (12).

A moment's consideration will show, too, that binding agents such as gum or glue must increase the coefficient of static friction tremendously. The coefficient of static friction is a measure of the resistance to sliding motion of two surfaces at rest, and since the nature of a binding agent is to hold surfaces together, the coefficient of static friction must certainly increase when binders are added. In this connection it seems probable that static friction is of greater importance to prompt ignition than kinetic friction, which comes into play only after static friction has been overcome. Then, too, static friction is always much greater than kinetic friction.

The sensitizing effect of T.N.T. and of tetryl in chlorate mixtures is probably not the result of purely frictional phenomena. Organic substances of this type are quite soft, and if present in excessive amounts, will desensitize even chlorate mixtures. Furthermore, T.N.T. will not sensitize fulminate compositions containing no chlorate. Tetryl and T.N.T. act in a very specific way on chlorates, and the investigation of this action offers another problem to the explosives chemist.

The disastrous effects of small amounts of oil or grease in priming mixtures are well known, and need not be enlarged upon. The effect is purely lubrication of the particles and elimination of friction within the pellet.

Some semi-quantitative experiments were made to determine how much energy is necessary to fire the standard .30 caliber F. A. 70 primer, and it is believed that the results confirm the idea that primer ignition is a purely surface phenomenon

originating in the solid interfaces of the composition. By running the drop tests on loaded primers and dummy primers, and comparing the depths of indentation caused by the firing pin, it was found that about 0.5 inch-ounce of energy is needed to fire the primer, the rest of the energy being used to deform the cup. It had been found previously that potassium chlorate and lead sulfoeyanide ignite at about 250°C., so that it was possible to calculate roughly the weight of material that had been heated. Assuming an average heat capacity of 0.2, the result turns out to be .000017 grams. Now since ignition is started in the portion of the pellet under the anvil point, only about one tenth of the pellet is actually under impact. And by assuming an average particle size of 10 to 20 microns, a reasonable figure, it is possible to calculate, in a very rough fashion, to be sure, the thickness of the heated layer on each particle. Such a calculation shows that if the .000017 gram of material is uniformly distributed over particles of 10 to 20 microns in diameter, the number of particles being one-tenth the number in the pellet, then the thickness of the heated layer is from 20×10^{-8} to 40×10^{-8} cm. The diameter of potassium chlorate and lead sulfoeyanide molecules is about 6×10^{-8} cm., so that the result obtained is of the right order of magnitude and supports the idea that primer ignition is primarily an affair between surface molecules.

Ignition Temperatures

Since priming mixtures are generally assumed to ignite through the agency of heat of internal friction, it becomes important to inquire into the temperature at which ignition takes place. Properly speaking, explosives do not possess a sharply defined ignition temperature in the same sense that they possess melting points or densities. On heating explosive materials at constant temperatures, there is encountered a more or less well defined range of temperatures in which decomposition sets in at an appreciable rate, leading finally to ignition or "puffing off". As the temperature is increased, the initial period of quiet decomposition is decreased, until a temperature is finally reached where true ignition is practically instantaneous. The theory of this phenomenon has been discussed by Garner (13), and will not be reviewed here.

An alternative method of determining ignition temperatures, one that is widely accepted, is to begin heating the material at a temperature well below the ignition point. The temperature is then increased at a constant rate until ignition takes place. The results obtained by this method are largely influenced by the amount of decomposition taking place before ignition occurs, and in this respect the procedure is said to be of value in showing up unstable smokeless powders. Under actual

conditions of use, however, explosives are subjected to instantaneously developed temperatures, rather than slowly rising ones, and the first method is to be preferred for investigating "true" ignition temperatures.

Taylor and Rinkenbach (10) determined the ignition temperatures of a large number of initiating explosives. Their procedure was to drop the sample onto a bath of Wood's metal held at a constant temperature, the time of ignition being noted. The point at which ignition occurred within one second or less was taken as the ignition temperature.

Similar experiments have been made at Frankford Arsenal, using a vertical tubular electric furnace. A two-hole plug in the top of the furnace is provided with two metal tubes which serve as holders for glass tubes, which may be renewed. One of the glass tubes carries a thermo-couple; the other receives the samples. After constant temperature has been reached, the samples are dropped into the furnace in the form of pellets and the time of ignition noted. A clean tube is used for each pellet.

So far, only initiating explosives and binary mixtures of fuels and oxidizers have been investigated, most of these being common priming ingredients. In many cases fairly well defined curves can be drawn for time of ignition vs. temperature. Some samples, however, behaved inconsistently, and it was very difficult to decide where to draw lines through the points. The short vertical lines at the top of each graph indicate temperatures at which samples failed to ignite within 30 seconds. Unless otherwise noted, 200/- mesh material was used in all mixtures.

The results for potassium chlorate with four fuels are shown in Figure 30. On comparing the lead sulfocyanide and stibnite curves, it becomes evident that the lead salt is the active fuel in the F.A. 70 type of mixture, since it ignites about 150° below stibnite. This is in accordance with the performance of some experimental priming mixtures in which lead sulfocyanide and stibnite were used separately with potassium chlorate. It was proved that stibnite might be omitted in chlorate mixtures, but that the lead salt was indispensable. Cuprous sulfocyanide ignites slightly above the lead compound, and zirconium is the least inflammable of the four. Its curve begins to slope off at 400°, and had the data been extended further, it undoubtedly would have approached the temperature axis as an asymptote. For comparison, two pyrotechnic compositions have been included; strontium and barium peroxides with magnesium. These also slope off, and their high ignition temperatures are in line with their insensitivity to impact.

Barium nitrate mixed with the same fuels is shown

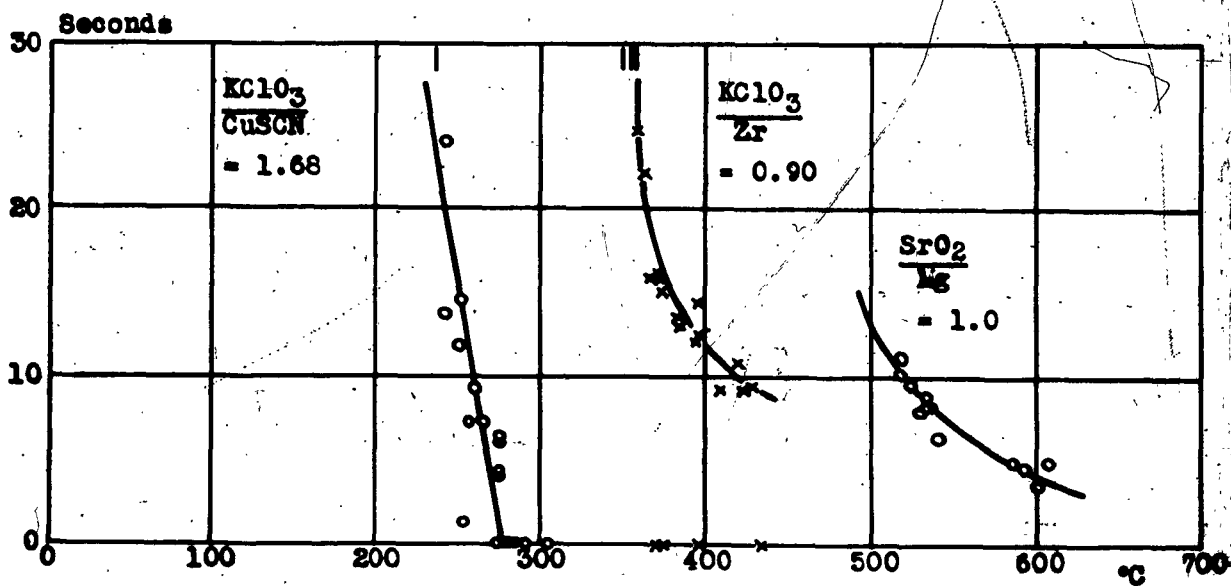
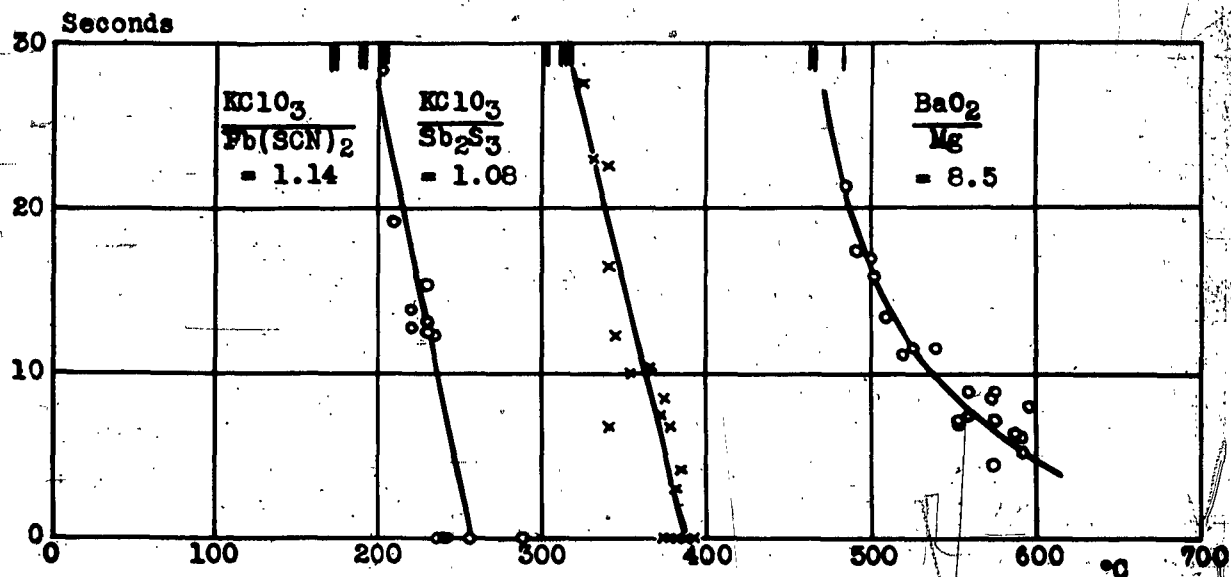


FIGURE 30

in Figure 31. Zirconium appears in this case to be quite equal to lead sulfocyanide, and both are far superior to stibnite. This, again, is in agreement with results obtained from mercury fulminate mixtures in which the stibnite had been replaced by zirconium or lead sulfocyanide. Cuprous sulfocyanide is almost as difficult to ignite with barium nitrate as stibnite. It should be noted that barium nitrate is quite effective as potassium chlorate in igniting zirconium, but that it lags far behind on the other three fuels.

Potassium perchlorate mixtures are shown in Figures 32 and 33. The data obtained with salt is unsatisfactory from the standpoint of curve tracing, especially the lead sulfocyanide mixture. But the relative positions of the points serve well enough for comparisons. Potassium perchlorate is more stable than the chlorate, and so it might be expected to give higher ignition temperatures. This is, indeed, the case for mixtures with stibnite and the sulfocyanides. The zirconium mixture, however, is a decided exception in that its curve lies at least 50° below the zirconium-chlorate curve. Apparently, ignition temperatures depend entirely on the combination being studied, and cannot always be inferred from the previous behavior of each constituent with other fuels and oxidizers. The curve for cuprous sulfocyanide and potassium perchlorate is a good example of a poor combination from the standpoint of inflammability. This curve approaches the temperature axis so slowly that it is doubtful whether prompt ignition would occur at any temperature less than about 700° . In this respect it ranks with the barium nitrate mixtures, so far as the data for these shows. Barium nitrate mixtures, of course have to be used with an initiating explosive.

The results for four initiating explosives are included in Figures 32 and 33. These curves are remarkably similar in their abrupt drop toward the temperature axis. Diazol checks very closely with mercury fulminate, both giving instantaneous ignition at about 260° . Lead styphnate lies about 70° higher. No doubt, this helps to account for the insufficient sensitivity of this salt in .30 caliber primers. The curve for tetracene also helps to explain why this material will overcome the insensitivity of lead styphnate mixtures. Tetracene shows a somewhat lower ignition temperature than mercury fulminate. In attempting to correlate ignition temperatures with sensitivity, a considerable mental reservation should be made concerning the effects of changes in the coefficient of friction, as noted in the section on friction.

Four strontium nitrate combinations appear in Figure 34. Mixtures of the sulfocyanides with strontium nitrate check very closely the same mixtures with barium nitrate, which might be ex-

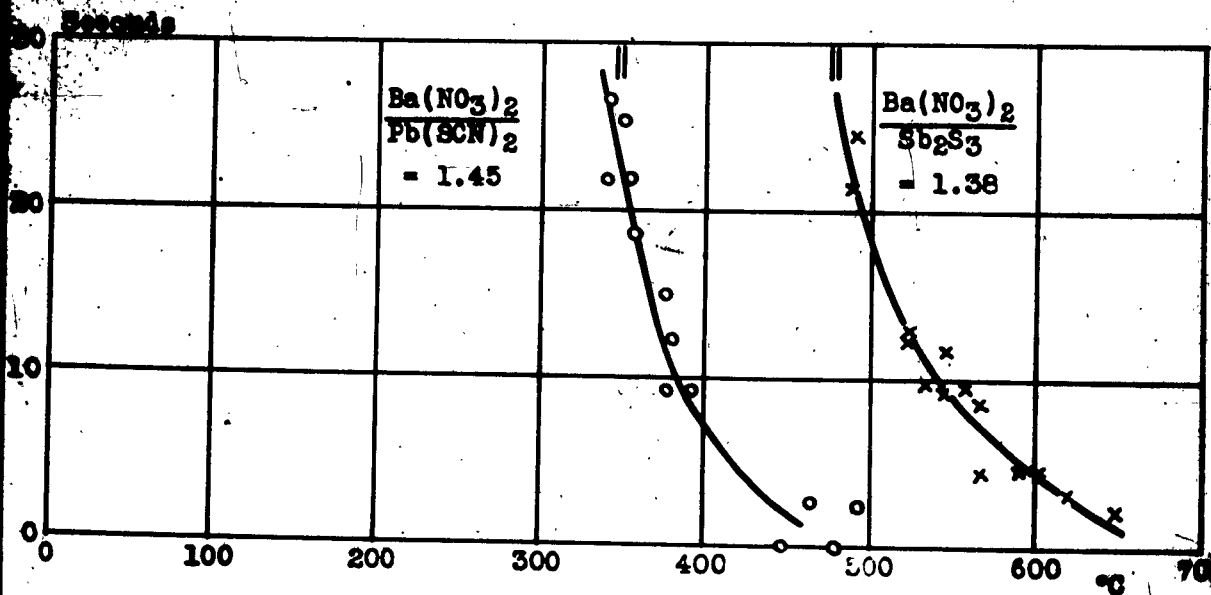
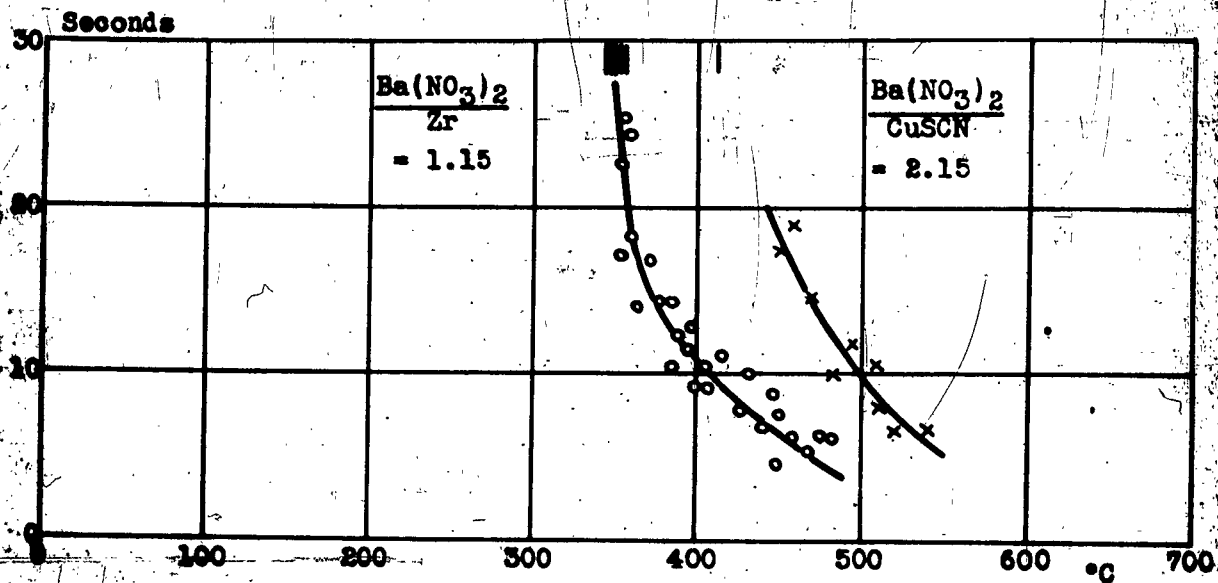


FIGURE 31

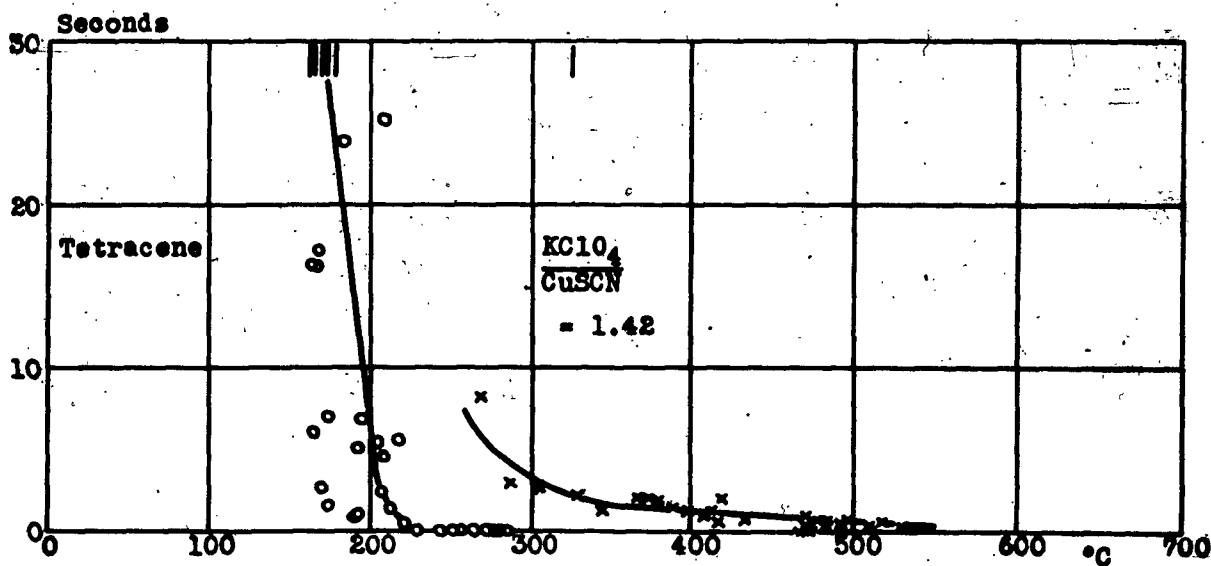
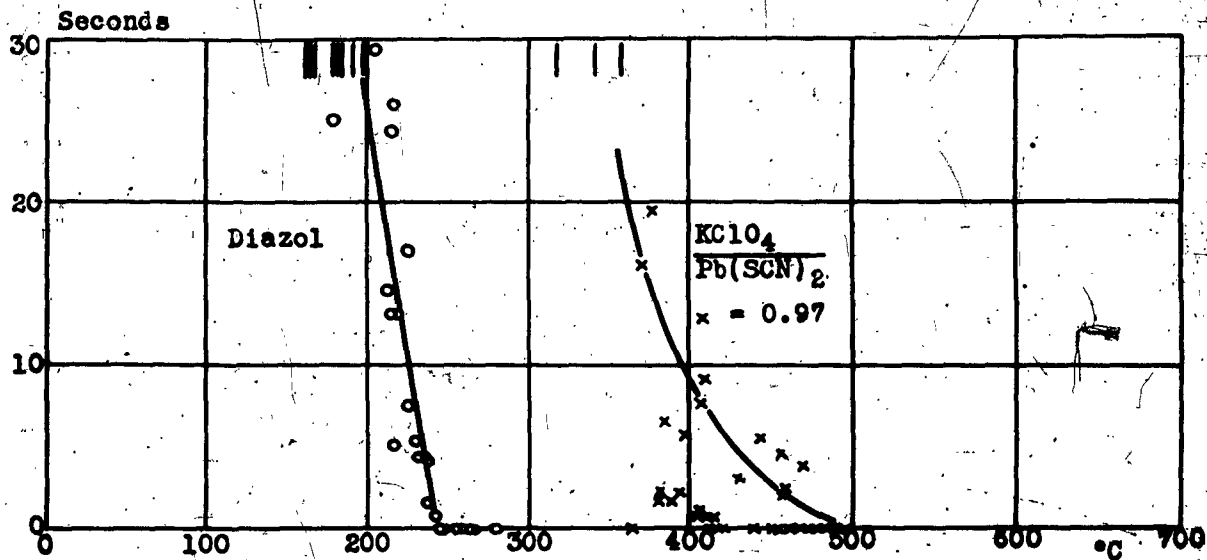


FIGURE 32

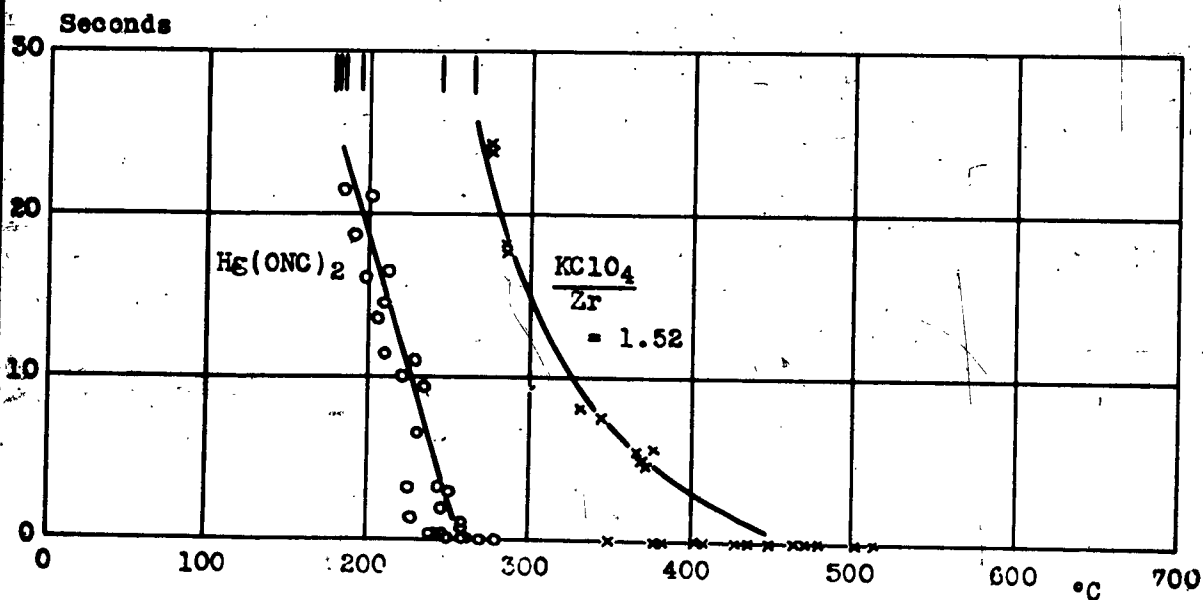
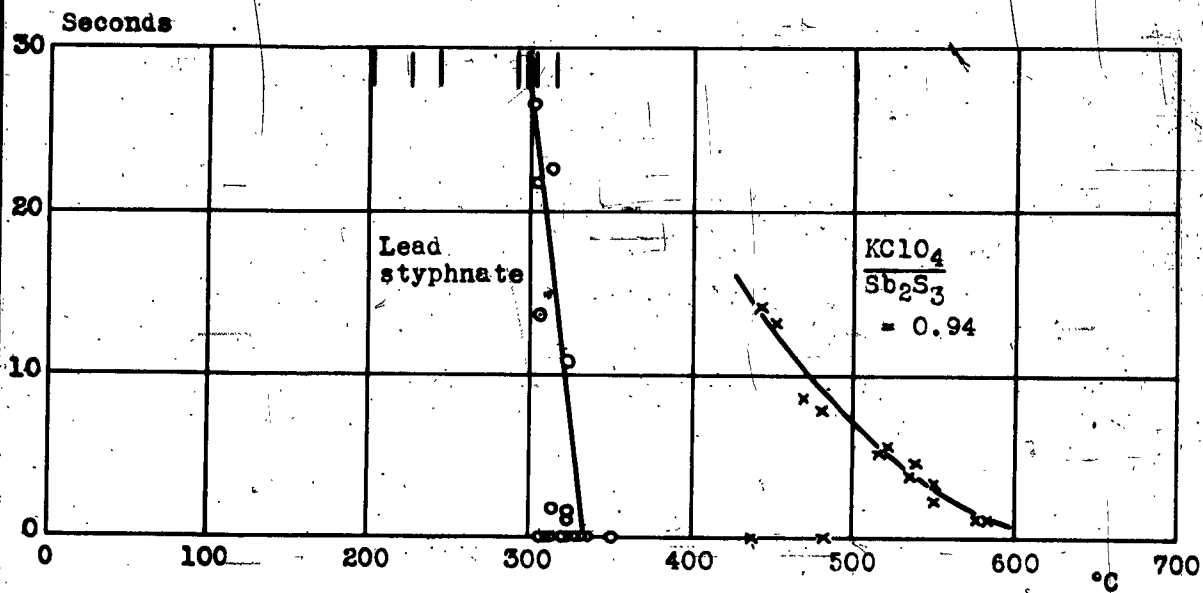


FIGURE 33

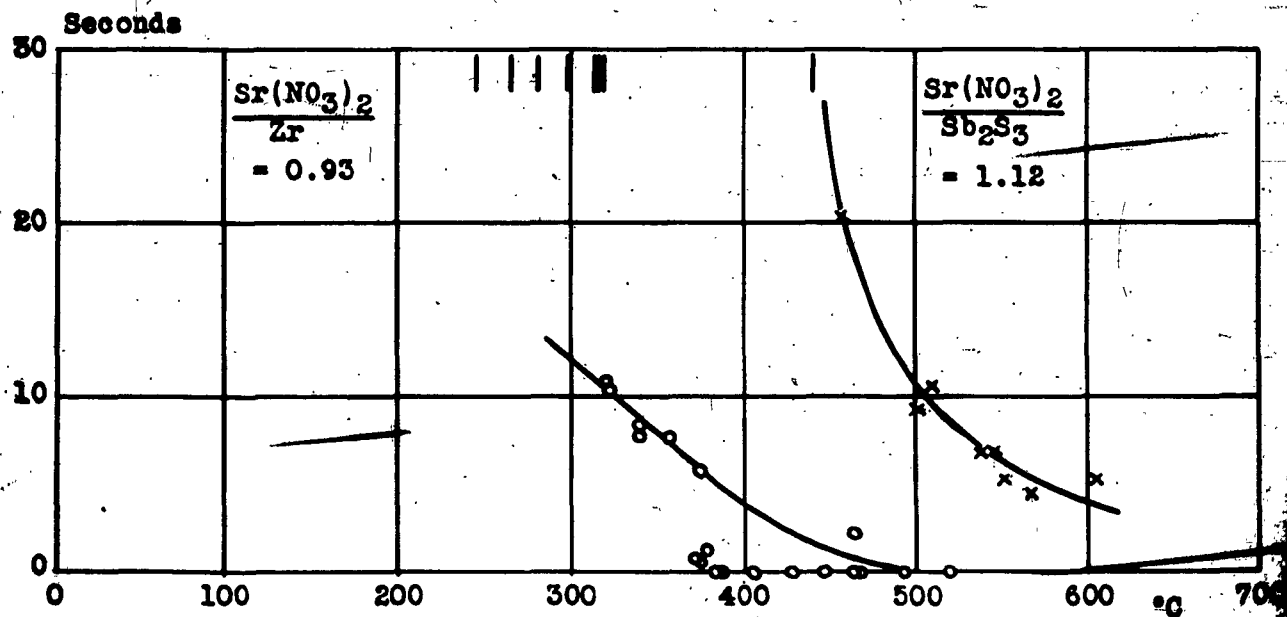
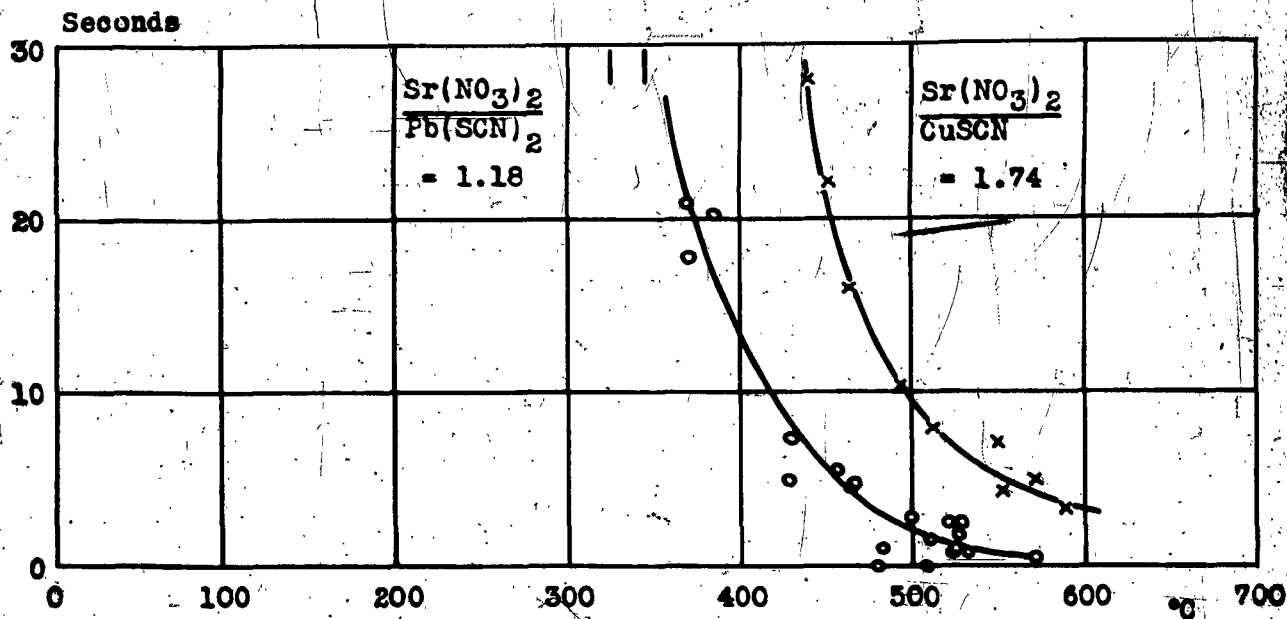


FIGURE 34

pected in view of the similarity between strontium and barium compounds. The strontium salt with zirconium and stibnite is only slightly easier to ignite than the same mixtures of barium salt. The small difference between strontium and barium nitrates in this respect probably explains why the substitution of strontium for barium in the 353-D mixture met with so little success, even though the heat of combustion should have been increased thereby. Apparently, there is little to be gained in case of ignition through the use of strontium nitrate instead of barium nitrate, at least for the four fuels investigated.

Some lead peroxide mixtures are given in Figure 35. The most interesting feature here is the marked difference between the lead sulfocyanide and copper sulfocyanide combinations, a difference shown by these fuels with no other oxidizer. The data from the lead sulfocyanide mixture is rather erratic, but the trend toward the region of sensitive materials like mercury fulminate is unmistakable. This peroxide-sulfocyanide combination deserves further study; it seems to suggest a new kind of non-corrosive non-fulminate composition of unsuspected possibilities. The curves in Figure 35 show again that ignition temperatures are quite unpredictable. Aside from the difference noted above, stibnite is more easily ignited by lead peroxide than by potassium perchlorate, but the reverse is true for cuprous sulfocyanide.

An unexpected result was obtained by varying the granulation of the potassium chlorate-stibnite mixture to 150/200 and 100/150 mesh. The sieve fractions used in these mixtures were obtained from the same sample of material, yet the curves in Figure 36 show a wide divergence of the 150/200 mesh mixture from the other two granulations. Naturally, this cannot be explained on the basis of contact surface between the ingredients, or adsorption of water vapor on their surfaces, for the 150/200 mesh material is intermediate in this respect with the other two granulations. It has not been determined whether the same behavior may be observed in other oxidizers and fuels, and no explanation will be offered until the matter has been investigated further. The effect, however, is of more than passing interest.

It is interesting to note that all compounds and mixtures used successfully to initiate combustion in the primer pellet give an almost perpendicular curve cutting the temperature axis below 275°. Specifically, the potassium chlorate-lead sulfocyanide mixture, diazot, mercury fulminate, and tetracene have this property. Lead styphnate also gives a curve which drops quickly toward the temperature axis, but its intersection is somewhat above 300°, and this fact seemingly is sufficient to place it just outside the pale.

The data on ignition temperatures that have been presented is convincing proof that explosives have no definite ignition temperature. The term "ignition temperature" is quite meaningless until it has been surrounded by many arbitrary test conditions. However, the method used in the present work for comparing ease of ignition is quite free of arbitrary conditions, even though it does not yet afford a definition of "ignition temperature". The plotting of time vs. temperature gives a curve, sometimes a vaguely defined one, which can, nevertheless, be compared with other curves as to position, slope, etc. The theoretical significance of such curves is not yet clearly understood, and the cause of some of the extremely erratic results cannot yet be explained. A study of these would probably throw considerable light on the behavior of priming compositions.

The Primer Flame

The most striking feature of flames in general is their high temperature, and many attempts have been made to relate the ballistic properties of primers to their flame temperatures, which have been either measured or calculated. Calculated temperatures are misleading for several reasons:

1. The reactions which are assumed in the calculations have never been proved to take place, and side reactions are ignored completely.
2. Those reactions which do take place never go to completion for appreciable amounts of the original ingredients may be found in the residue.
3. The flame is always cooled to some extent by its rather devious passage over metal surfaces. The unreacted particles blown out of the primer absorb heat from the flame, and cool it still further.

Borland (14) attempted to measure flame temperatures by recording radiation intensities on photographic plates, comparing the intensities with a standard radiant whose temperature was known. The duration of the flame and its effect on the recorded intensities was neglected, however, and it is doubtful whether the results are entirely comparable. Borland realized that the flame temperature is constantly changing due to heat exchange with metal surfaces and unreacted ingredients; so it is difficult to see how the term can have any definite meaning so long as various parts of the flame are at different temperatures.

The important thing, of course, is to have a rapid

exchange of heat from the flame to the propellant, and any change in the primer which facilitates the exchange of heat should improve the ballistics of the ammunition. It is important, too, to have a fairly constant rate of heat exchange, in order that uniform ballistics will be obtained. The most obvious way to increase the rate of heat exchange would be to increase the speed of combustion of the primer pellet. The flame is then driven further into the powder charge, the cooling effects previously noted are reduced, and most important of all, the hot gases sweep over the powder grains with greater velocity and heat them up to ignition more quickly. The disadvantage of using a high speed primer is that high local pressures are built up in the primer cup, causing set-back and leaks. This effect has been noted in certain fulminate compositions containing large amounts of zirconium.

Fortunately, there are other ways to facilitate heat exchange which can be easily shown. Taking a simple case of heat transfer from a hot body to a cold body, the total heat capacities of both bodies being finite, it can be demonstrated that the rate of temperature rise of the cold body is

$$\frac{dT}{dt} = a + bT \quad \text{----- (4)}$$

where T = temperature of the cold body at any time t,

$$a = K \left\{ \frac{S}{C} + \frac{S'}{C'} \right\} .$$

$$\text{and } b = - K \left\{ \frac{1}{C} + \frac{1}{C'} \right\} .$$

K is the overall coefficient of heat transfer from the hot to the cold body, S and S' the initial temperatures of the cold and hot bodies respectively, and C and C' the total heat capacities of the cold and hot bodies respectively.

In the case of ignition in ammunition, the hot body, of course, is the primer flame and the cold body is the propellant charge. The important thing to note is that the heat capacity of the primer flame is an important variable governing the rate of heating of the propellant charge. Moreover, the flames from various compositions may vary widely in their heat capacities. Some of the common gaseous constituents of primer flames are listed in Table 7 with their specific heats in calories per gram at constant volume.

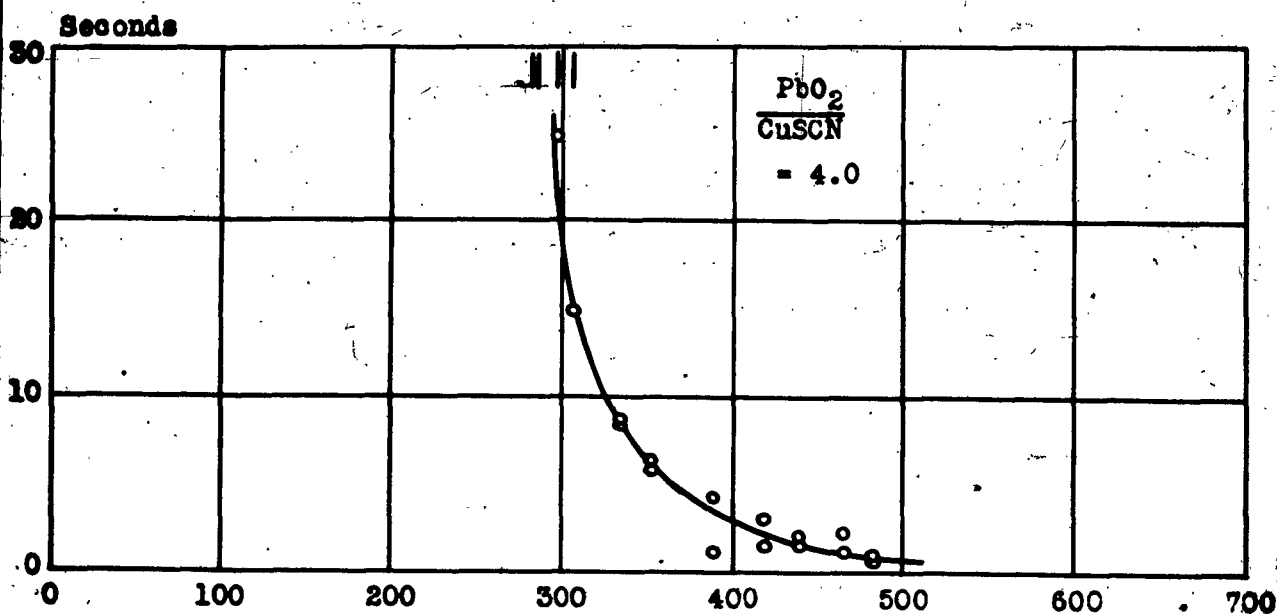
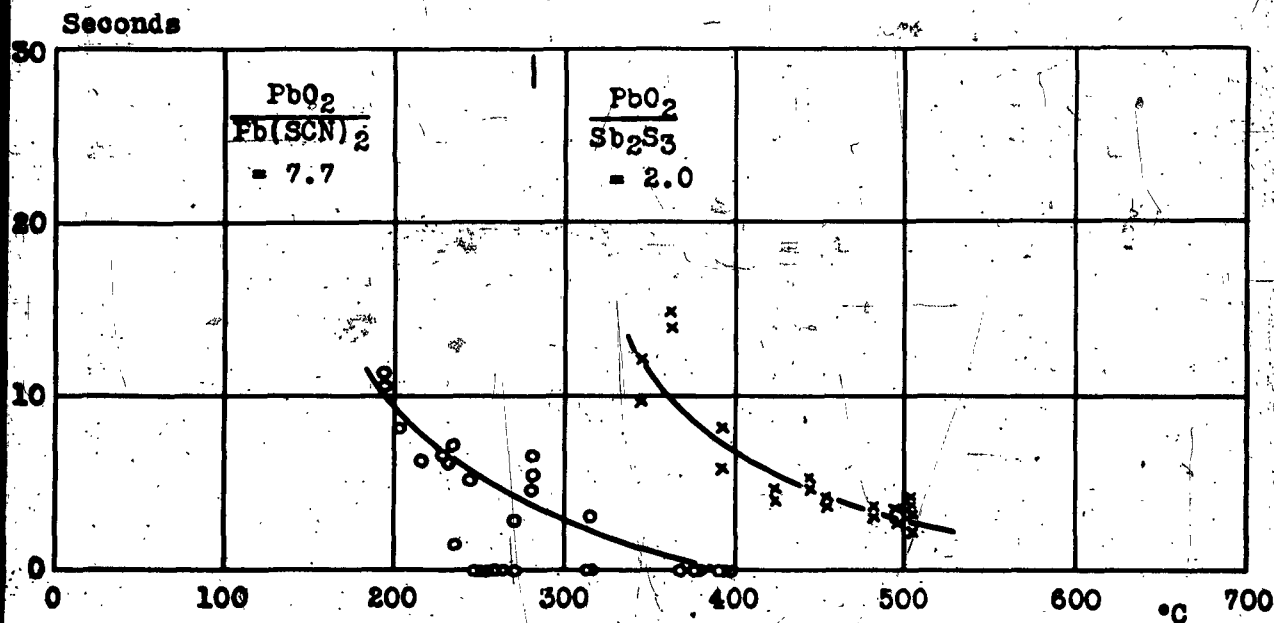


FIGURE 35

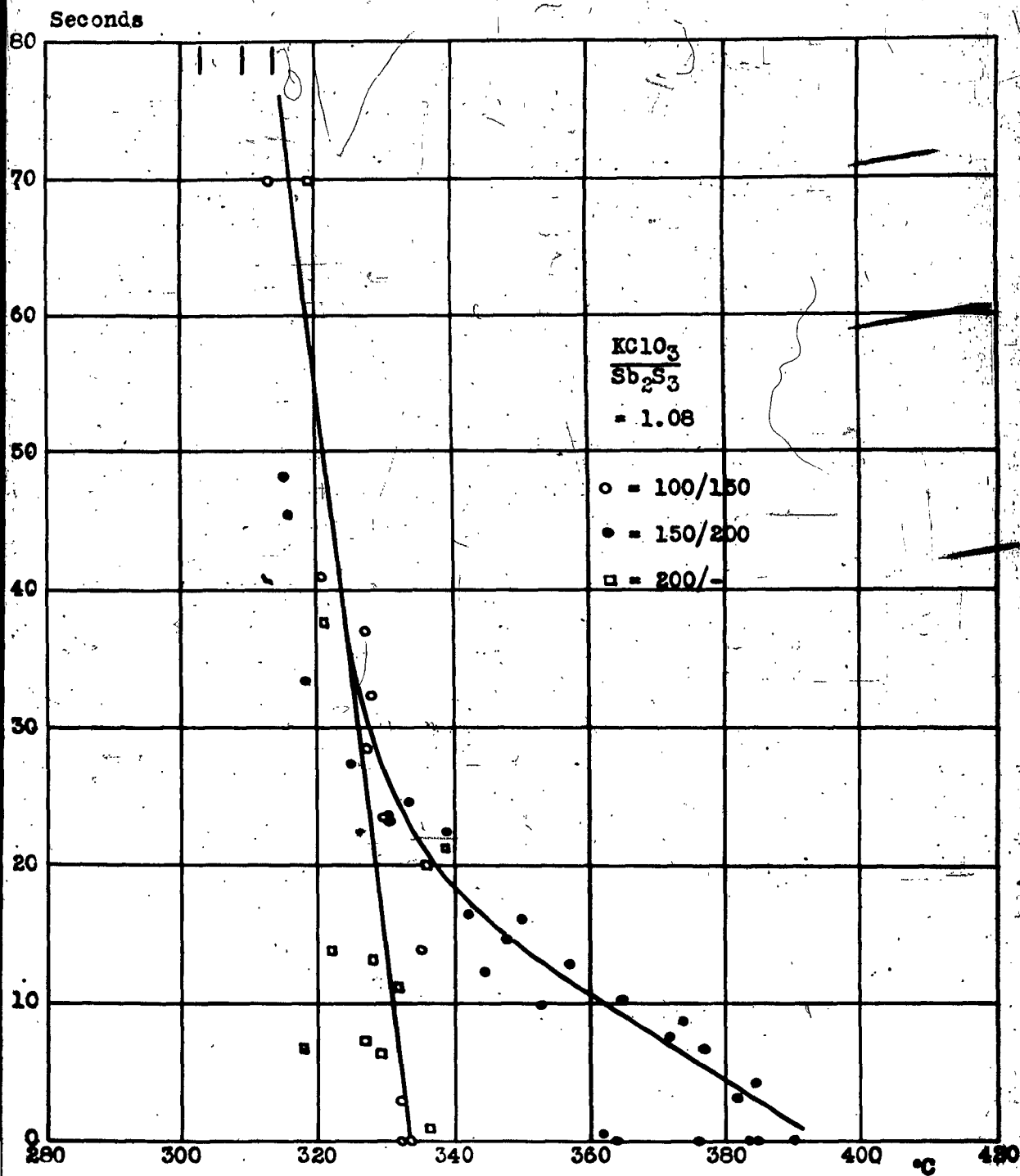


FIGURE 36

Table 7

C_v at 1000°C.

Hg vapor	.015
N ₂	.195
CO	.195
CO ₂	.231
SO ₂	.231

On integrating Equation 4, the temperature of the cold body may be expressed as a function of time:

$$T = \left\{ \frac{a}{b} + s \right\} e^{bt} - \frac{a}{b} \text{ ----- (5)}$$

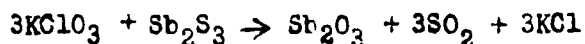
By means of Equation 5 it is now possible to draw curves showing the rate at which the gases in Table 7 will heat up an equal weight of nitrocellulose. Figure 37 shows such curves in which the temperature of the cold body, or nitrocellulose, is plotted against time. The nitrocellulose is taken at an initial temperature of 20°C., specific heat 0.3, the gases being heated to 1000°C. The curve shows that under the stated conditions, the mercury vapor is totally unable to ignite the nitrocellulose, while the other four gases cause a prompt rise in temperature. Carbon dioxide and sulfur dioxide are slightly better than nitrogen and carbon monoxide, but the difference is negligible.

These results lead naturally to a consideration of the part played by solid and molten matter in the primer flame. An exact quantitative comparison with gases is not possible, however, due to the uncertainty regarding K, the overall coefficient of heat transfer. K may be considered constant in the comparison of gases, and to simplify matters it was made equal to unity in calculating curves for the gases. But when heat flows from solid to solid or from liquid to solid, the character of the flow changes and, quite generally, K increases greatly. The increase may be anywhere from ten-fold to one hundred-fold (15). And since K always increases when solids or liquids are substituted for gases, it is believed that theory is not being strained by drawing curves for molten potassium chloride and stibnite (Figure 37). The coefficient K was taken ten times as great as for gases, for the sake of being conservative, and specific heats of 0.16 for potassium chloride and 0.09 for stibnite were used (16). The curves are only approximate, but they show plainly, in spite of the conservative assumptions, that molten and solid matter in the flame is much more effective than any of the gases in promoting ignition.

The importance of having "incandescent particles" in the primer flame has been argued pro and con for many years without the question ever having been settled definitely. The examination of primer residues suggests that droplets of molten matter are more in evidence than incandescent particles, and that these would certainly cling to powder grains more tenaciously than solids. However that may be, it is fairly certain from the foregoing discussion of specific heats that either molten or solid matter will promote ignition more quickly than gases at the same temperature. Some of the work recently done at Picatinny Arsenal (17) shows that from 60% to 70% of the primer flame is solid or liquid matter, the rest being gases. So that all the evidence, both experimental and theoretical, seems to point to solid and liquid matter as an overwhelmingly active agent in primer flames. It is probable, then, that the only reason for having any gas at all in the flame is to get a sufficiently high pressure in the cartridge case at the moment the propellant charge is ignited. The speed of combustion of the charge depends, as everyone knows, on the pressure, so that a primer which fails to give off a sufficient amount of gas may cause hangfires quite as easily as one which does not yield a sufficient amount of molten matter.

Experiments are being planned for investigating residues from primer flames in order to determine approximately the structure of the flames. Preliminary work has shown that the distribution and degree of subdivision of liquid and solid matter in the flames can vary widely with different compositions. The F.A. 70 mixture gives a uniform spray of potassium salts and stibnite. Certain fulminate mixtures, on the other hand, produce a very fine cloud of solid barium oxide and a few scattered drops of molten barium nitrate and stibnite. The bearing such a difference might have on the ignition of smokeless powders is obvious.

In the determination of ignition temperatures, it was found that pellets of potassium chlorate and antimony sulfide gave reddish brown residues which were strongly acid. Now the reaction ordinarily assumed for these compounds is



and of course neither of the solid products, potassium chloride or antimony oxide, is strongly acid or colored. Subsequent experiments proved that a secondary reaction takes place between potassium chloride and unburned stibnite with the formation of reddish brown potassium polysulfide and antimony chloride. The latter compound then hydrolyzes in water to give hydrochloric acid. The question of interaction between potassium chloride and antimony oxide has been raised (14), but no evidence of it was found by this Laboratory. It can be shown, however, that

the same kind of reaction takes place in mixtures of lead sulfocyanide and potassium chlorate. The lead salt seems to lose cyanogen gas, which is burned by the chlorate; the residue of lead sulfide and potassium chloride then yields potassium sulfide and lead chloride, which reacts acid.

Several .30 caliber primers loaded with the F.A. 70 mixture, which contains chlorate, stibnite, and lead sulfocyanide, were fired into an airtight flask containing a little water. A simple titration with standard alkali showed that the average pellet yields 1.71 milligrams of hydrogen chloride on explosion, while the same experiment with fulminate primers showed that no acid is formed. This result is highly significant from the standpoint of corrosion in rifle barrels, for the general opinion since 1920 has been that potassium chloride is solely responsible (3). This would seem to revive the whole question of what constitutes a corrosive primer, since it ought to be possible to get neutral or alkaline residues from chlorate mixtures by eliminating fuels which give acid residues. The subject deserves to be investigated.

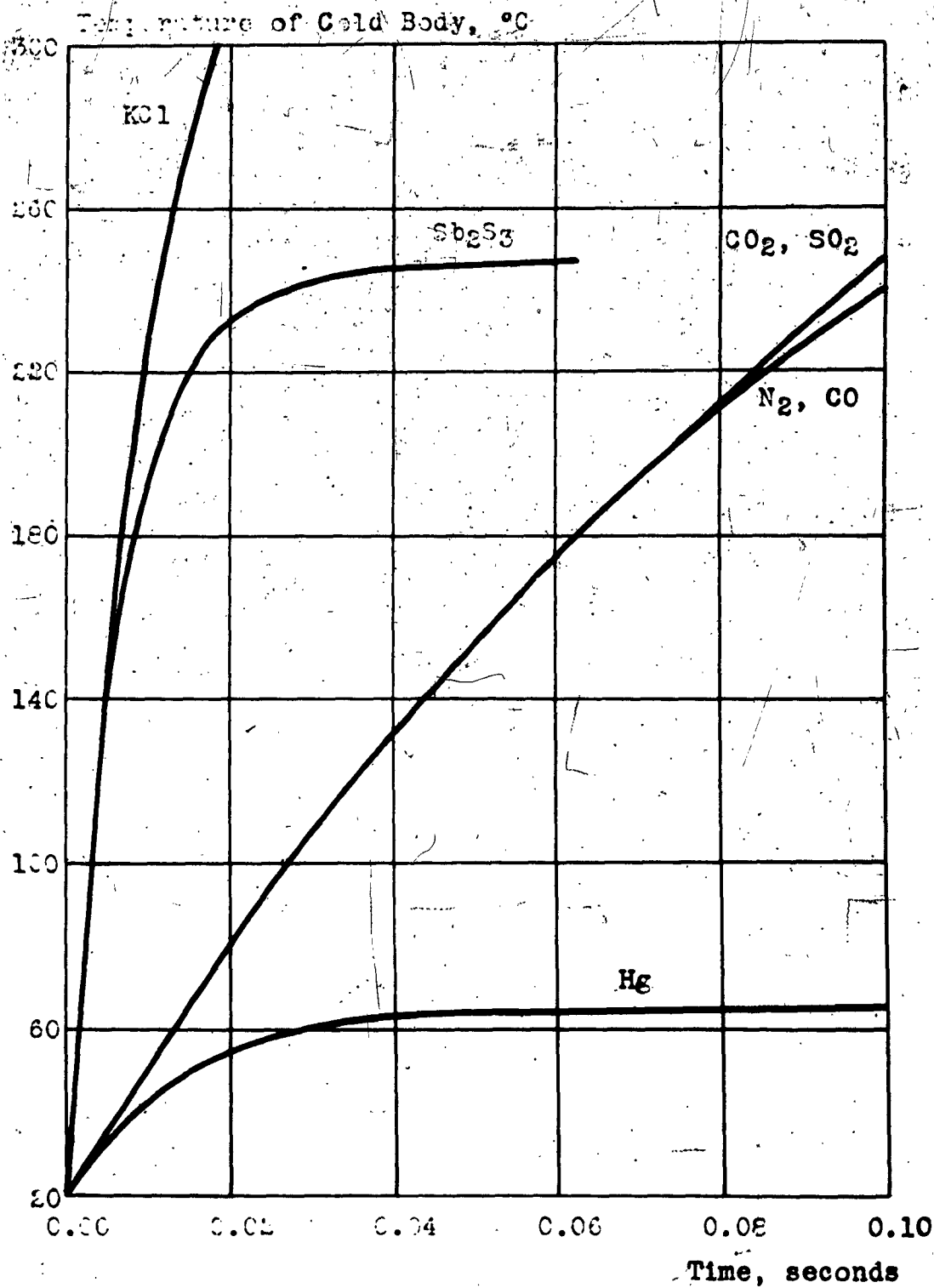


FIGURE 37

IV. CONCLUSIONS

1. Strontium nitrate and normal lead nitrate show no advantage over barium nitrate in fulminate mixtures of the 353 type.
2. Cuprous sulfocyanide shows no advantage over lead sulfocyanide in the 353 type of fulminate mixture. When used in wet mixture of this kind, rapid decomposition sets in.
3. Barium nitrate crystals coated with potassium permanganate, trinitrotoluene, pentaerythrite tetranitrate, or picric acid do not improve dry fulminate mixtures. On the contrary, a marked drop in sensitivity takes place with the last three compounds.
4. Tetracene cannot be used as a substitute for mercury fulminate.
5. Mixtures containing mercury fulminate and lead styphnate or basic lead picrate have not been successful so far.
6. Compositions containing mercury fulminate and lead styphnate or basic lead picrate are desensitized by wet loading.
7. Dry mercury fulminate compositions containing lead styphnate are more violent than those containing basic lead picrate, a strong tendency toward pierced primers being noticeable.
8. Dry mercury fulminate compositions containing lead styphnate have less tendency to hangfire than those containing basic lead picrate.
9. Wet mercury fulminate mixtures containing lead styphnate give a better hangfire test than those containing basic lead picrate.
10. Wet mercury fulminate mixtures containing either lead styphnate or basic lead picrate show a strong tendency to misfire under full machine gun action. These compositions are generally inferior to the dry charged mixtures.
11. In the 353-D type of fulminate mixture, the best hangfire tests are obtained by using 150/200 mesh barium nitrate and 200/- mesh antimony sulfide.
12. Mercury fulminate mixtures of the 353 type show a greater tendency to hangfire when loaded wet than when loaded dry. The reverse is true when the lead sulfocyanide is increased

to 15% or more, the dry mixtures then giving the greater number of hangfires.

13. Mercury fulminate mixtures of high lead sulfocyanide content, containing no antimony, are quite useless unless loaded wet.

14. A very promising non-corrosive ternary mixture (402-W) can be prepared from mercury fulminate, barium nitrate and lead sulfocyanide. The hangfire test of this mixture is comparable with that of the F.A. 70.

15. By gradually substituting zirconium for lead sulfocyanide in the ternary mixture 402-W, a whole series of non-corrosive compositions can be prepared, none of which have given lags or hangfires under full machine gun action.

16. By substituting zirconium for lead sulfocyanide in the ternary mixture 402-W, the speed of combustion is apparently increased, and when more than 10% zirconium is used, a strong tendency toward leaky primers is observed.

17. The best proportion of zirconium to use in four-component, 20% fulminate mixtures is approximately 10%, the other ingredients being barium nitrate and lead sulfocyanide, and the whole adjusted to approximate oxygen balance.

18. The four-component 403-W type of mixture, containing 10% zirconium and 20% fulminate, may have its fulminate content varied from 15% to 25% without affecting the ballistic properties of the composition.

19. The four-component 394-W type of mixture, containing 20% zirconium and 20% fulminate, yields lags and hangfires when its fulminate content is either decreased or increased.

20. In order to avoid hangfires in the four-component fulminate mixtures containing zirconium, the granulation of the barium nitrate must be at least as fine as 200/- mesh.

21. The sensitivity and ballistic effects of mercury fulminate compositions are distinctly poorer when either fine or coarse fulminate is used exclusively. It is necessary to have both fine and coarse mercury fulminate present.

22. The F.A. 70 type of mixture is not appreciably affected by coating the potassium chlorate crystal with potassium permanganate.

23. Tetracene cannot be used in place of T.N.T. for sensitizing the F.A. 70 type of mixture.

24. The ballistic performance of the F.A. 70 composition is not affected by varying the granulation of the potassium chlorate and antimony sulfide through the 100/150, 150/200, 200/- mesh sieve fractions, using all nine of the possible combinations.

25. The ballistic performance of the F.A. 70 type of mixture is very much impaired by dry charging, which causes a marked tendency to hangfire.

26. The sensitivity and ballistic effects of the F.A. 70 composition are not altered noticeably by leaving out the stibnite altogether.

27. The ballistic performance of the F.A. 70 composition is apparently unchanged when both stibnite and T.N.T. are omitted, but the absence of T.N.T. causes a sharp decrease in sensitivity.

28. The Rathsburg composition containing tetracene and lead styphnate is definitely impaired by wet loading.

29. The Rathsburg composition containing basic lead picrate in place of the styphnate is desensitized by wet loading.

30. Tetracene has a marked sensitizing effect on the Rathsburg mixture containing either the basic picrate or styphnate of lead.

31. Basic lead picrate is inferior to lead styphnate in the Rathsburg primer.

32. The Rathsburg primer is equivalent to the mercury fulminate primer from the standpoint of sensitivity and hangfires. It has the advantage that no mercury is present in the mixture; its chief disadvantage is the danger of handling lead styphnate.

33. Diazol shows promise as a substitute for mercury fulminate.

34. Antimony sulfide is of little value as fuel or abrasive; its chief function is probably that of heat carrier as shown in the section on the Primer Flame.

35. No general rules can be given for the effects of wet charging on the performance of primers. The effects of wet charging are specific for each composition.

36. According to theory, the sensitivity to impact of a binary mixture of fuel and oxidizer should vary with the particle size ratio of the one to the other.

37. According to theory, the speed of combustion of any inflammable mixture should vary with the absolute granulation of the ingredients.

38. According to theory, the observed discrepancy between ignition temperatures and impact sensitivities of explosive materials is caused by variations in the forces of friction between the crystals.

39. No general rules can be drawn for predicting the ease of ignition of a binary mixture of oxidizer and fuel. The ease of ignition is peculiar to each mixture.

40. Among the samples studied, the ignition temperature curves for initiating explosives and mixtures that are sufficiently sensitive for .30 caliber primers were all similar, and intersected the temperature axis at or below 275°C.

41. The ignition temperature curve for a mixture of potassium chlorate and stibnite depends in some unknown way on the granulation of the ingredients.

42. According to theory, the rate of heat exchange between primer flame and propellant charge depends on the heat capacity of the flame. In this respect, nitrogen, sulfur dioxide, and the oxides of carbon are superior to mercury vapor. Because of the greater overall coefficient of heat transfer, solid or molten matter is more effective than gases.

43. The function of gas in the primer flame is not to ignite the powder grains, but to create a sufficiently high pressure at the moment ignition occurs.

44. The corrosive action of chlorate primers on rifle barrels is due, at least partly, to the liberation of hydrochloric acid during explosion.

V. RECOMMENDATIONS

1. The non-corrosive, three-component mixture containing mercury fulminate, barium nitrate, and lead sulfocyanide should be investigated further.
2. The non-corrosive, four-component mixture containing mercury fulminate, barium nitrate, lead sulfocyanide, and zirconium should be investigated further.
3. Experimental mixtures should be made with diazot, tetracene, and possibly basic lead picrate, with the object of developing a non-mercuric, non-corrosive composition. Lead styphnate has a bad reputation as a hazard to life and limb, and is not favored in primer work.
4. The problem of eliminating stibnite from the F.A. 70 type of mixture deserves consideration, carefully weighing the advantages against the disadvantages. This would require an extensive loading and firing program.
5. The properties of graded microscopic powders and inorganic colloids in priming mixtures ought to be investigated with the object of increasing the activity of certain sluggish ingredients.
6. The relationship between granulation and the speed of combustion and sensitivity of priming mixtures should be determined. Information of this kind would help in regulating the speed of combustion of primers, and would offer a valuable check on the theory of granulation.
7. The possibility of altering coefficients of friction between crystals by means of adsorption phenomena should be investigated with the object of altering sensitivity to impact. Wherever possible, the theory of friction forces in sensitive mixtures should be checked experimentally.
8. The sensitizing effect of small quantities of nitro-organic compounds on chlorate primers should be worked on, since it may lead to the sensitizing of sluggish oxidizers such as barium nitrate.
9. Ignition temperatures should be determined on additional binary and perhaps ternary mixtures. Those mixtures igniting below 275°C. seem well suited as initiating agents in .30 caliber primers, and it ought to be possible to pick out valuable combinations in this way.
10. According to ignition temperature curves, a mixture of lead peroxide and lead sulfocyanide ignites almost as easily as

the corresponding chlorate mixture. The value of this combination as the basis of a new kind of non-mercurous, non-corrosive composition ought to be investigated.

11. Experiments should be made on the use of new fuels, such as the ferrocyanides, cyanides, oxalates, etc. in both non-corrosive and chlorate primers.

12. In view of the appreciable quantity of hydrochloric acid liberated during combustion of the F.A. 70 composition, it would be highly desirable to determine to what extent this acid is responsible for the corrosion observed with chlorate primers in general.

13. The possibility of developing a chlorate primer which gives a neutral or alkaline residue is attractive. Such work should be correlated with the investigation of new fuels for ignition systems.

14. Experiments should be continued on determining the structure of flames with reference to the solid and molten matter present.

VI. SUMMARY

The results of sensitivity tests and hangfire tests have been described in detail for fifty-nine mercuric non-corrosive priming mixtures, twenty-three chlorate mixtures, and ten non-mercuric, non-corrosive mixtures.

The experimental mercuric non-corrosive compositions included the following lines of endeavor:

1. Substitution of strontium and normal lead nitrates for barium nitrate.
2. Substitution of tetracene for mercury fulminate.
3. Sensitizing barium nitrate with potassium permanganate, T.N.T., P.E.T.N., and picric acid.
4. Substitution of cuprous sulfocyanide for lead sulfocyanide.
5. Addition of lead styphnate and basic lead picrate to mercuric mixtures.
6. Effect of varying the granulation of barium nitrate and antimony sulfide.
7. Relative importance of lead sulfocyanide and stibnite as fuels.
8. Use of zirconium as a fuel.
9. Effect of varying the mercury fulminate content of zirconium mixtures.
10. Effect of varying the granulation of barium nitrate in zirconium mixtures.
11. Effect of varying the granulation of mercury fulminate.

On experimental potassium chlorate mixtures, the following work was done:

1. Sensitizing potassium chlorate with potassium permanganate.
2. Use of tetracene in chlorate mixtures.

3. Effect on the F.A. 70 mixture of varying the granulation of potassium chlorate and antimony sulfide.
4. Relative importance of lead sulfocyanide and stibnite as fuels.

On non-mercuric, non-corrosive mixtures the experiments included:

1. Sensitizing effect of tetracene in the Rathsburg primer.
2. Use of basic lead picrate in place of lead styphnate in the Rathsburg primer.
3. Substitution of diazot for mercury fulminate in non-corrosive mixtures.

The effect of wet and dry charging on all types of mixtures has been observed.

The theory of granulation has been considered. The condition for maximum sensitivity of a binary mixture of oxidizer and fuel has been expressed mathematically.

Ignition temperatures have been discussed. Experimental ignition temperature curves are given for twenty-five initiators and explosive mixtures.

The theory of coefficients of friction in priming mixtures has been discussed qualitatively.

The structure of the primer flame has been considered. An expression has been developed for the relative effectiveness of various primer flame constituents in promoting ignition of the propellant charge. Curves have been drawn for this expression showing that the specific heat of each primer flame constituent is an important variable governing the time required for ignition of the propellant charge.

The liberation of hydrochloric acid during explosion of the F.A. 70 primers has been demonstrated.

The possibility of developing a non-corrosive chlorate primer by a suitable choice of fuels has been pointed out.

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